Environment Canada | Environnement Canada

National Water Research Institute | Institut National de Recherche sur les Eaux

C.3

National Water Research Institute
Analytical Methods Division

Annual Study Reports
1982/1983

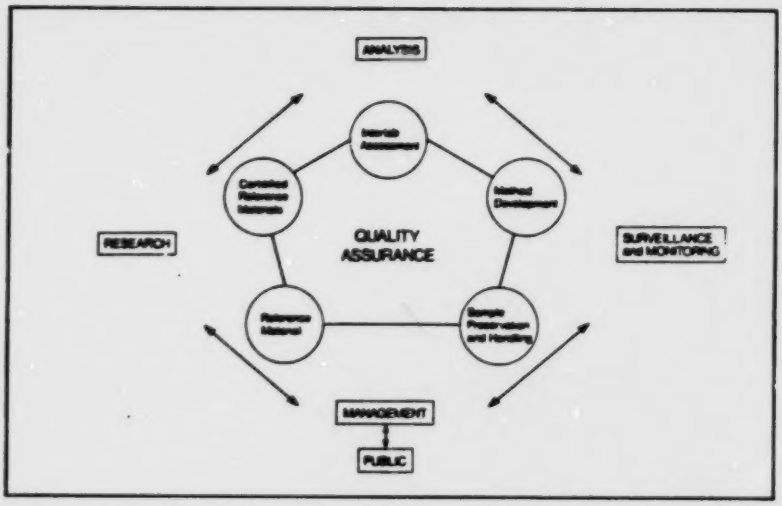
Analytical quality assurance: key to reliable environmental data

by J. Lawrence, A.S.Y. Chau and K.I. Aspila

The number of anthropogenic materials entering our environment is increasing. Many of these materials are hazardous to human health and incompatible with the ecosystem. Consequently, environmental protection and pollution control have become one of modern man's preoccupations. A prerequisite for decision making in environmental protection and pollution control is the ability to identify and measure these man-made materials in the environment. Nearly every phase of environmental protection depends on analytical data. However, it is not sufficient merely to generate data. The data must be reliable.

Generation of analytical data is expensive. It involves a considerable outlay of both human and financial resources for sampling programs and analytical equipment, and for the analysis and interpretation of data. The financial implications of decisions, which are based on analytical data, can be extremely large, such as whether to improve a sewage treatment process, or undertake plant modification or construction of new facilities, etc. Indeed, "never before have so many critical decisions involving health, safety and economics depended on the quality of chemical analytical data."[1]

To avoid irrational decisions, political embarrassment and financial loss because of questionable analytical data, an effective quality assurance program is essential to ensure the reliability of data.



Types of quality assurance

Quality assurance is usually divided into two classifications; intralaboratory and interlaboratory programs.

Intralaboratory quality assurance

The intralaboratory quality assurance program is a continuing and systematic regimen carried out by each of the analytical laboratories. It is the first step to ensure the quality of data. It provides a continuous check on the performance and capability of each analyst in the laboratory measurement process.

Due to its instrinsic and inherent characteristics, intralaboratory quality control can only reflect on the performance of each laboratory in isolation. There are several limitations. For instance, it cannot assess the comparability and compatibility of data or methods with other laboratories which contribute data to the same data banks or the same surveillance or monitoring program. Quite often, intralaboratory quality control does not provide information on how accurate the data are.

Interlaboratory quality assurance

The interlaboratory quality assurance program is usually conducted by an outside, neutral agency to assist analytical laboratories to assess their overall laboratory performance (including the effectiveness of their intralaboratory quality control program), and to ensure reliability and compatibility of data generated. In addition, an interlaboratory program, "indicates the degree of confidence which can be placed in the results of sample analyses." This last issue is most important to the users of data. In fact, it is unfortunate that those who use real data, those who manage programs, those who generate data, and those few who monitor quality do not often interrelate with a clear understanding of each others' requirements.

An effective interlaboratory quality assurance program should involve various activities to assist analytical laboratories to generate reliable data and should control all the areas that could affect the quality of analytical data. Distribution of test samples to participants and compilation of results in a report is only the final step of the program. Interlaboratory quality assurance programs consist of many research and investigative activities such as sample collection, preservation, transportation, as well as evaluation of analytical methodology. A repository of reference analytical standards for distribution to analytical laboratories is also required.

In addition, research to develop Certified Reference Materials (CRM's) and Reference Materials (RM's) for both organic and inorganic parameters in environmental substrates must also be undertaken to enhance the effectiveness of intra and interlaboratory quality control programs.

Analytical Methods Division, National Water Research Institute, Canada Centre for Inland Waters, Box 5050, Burlington, Ontario.

The key components of an effective quality assurance program are summarized in Figure 1. This diagram depicts the salient relationship and importance of quality assurance with other activities in environmental data collection and data use. Our quality assurance program is formulated according to the above concept: the key features are now discussed below.

Quality assurance at NWRI

At the National Water Research Institute, we conduct three types of interlaboratory quality assurance studies each with a different objective; (a) an interregional program for the five Regional Water Quality Branch Laboratories of Environment Canada; (b) a national program for government, university and private sector laboratories; and (c) an international program for all laboratories participating in the Canada-US Great Lakes Water Quality Agreement Programs. The total program involves over 190 laboratories. Almost 200 interlab studies have been completed over the past eight years.

Each analytical laboratory is responsible for its own internal quality control.

Interregional studies

This is the oldest part of our interlaboratory quality assurance program and involves only the five Water Quality Branch Regional Laboratories across Canada. These laboratories are responsible for monitoring the quality of surface water, sediments and other aquatic media on a national scale.

As an on-going activity, natural water and sometimes sediment samples, are distributed monthly for the analyses of a wide range of parameters routinely determined in the five regional laboratories. This program is designed to detect data anomalies and to correct them rapidly when found. To do this, the number of test samples and the data treatment and interpretation are kept to a minimum. The mean, standard deviation and relative standard deviation are calculated and any data which deviate statistically from the mean are flagged. These studies enable labs to compare their performance with other Water Quality Branch laboratories and to monitor the effectiveness of their-in-house quality control activities.

National studies

This program involves more than 100 laboratories in Canada including federal, provincial, university, and private sector laboratories. The results of these studies are usually published in the Reports Series of the Inland Waters Directorate, Environment Canada (copies may be obtained by writing to the authors).

The main purposes of these studies are:

(1) to assess the compatibility of analytical data and methodology between the Water Quality Branch laboratories and other laboratories particularly those labs using methods different from the WQB labs;

(2) to assist in the certification of our CRM's and P.M's;

(3) to evaluate contract laboratories for future analytical contracts; and

(4) to provide information to all participating labs on data compatibility on a national basis.

The program has traditionally addressed waters for major components (major ions, nutrients, trace metals and physical parameters). More recently, toxic organics are being addressed such as PCB in sediments and this trend is likely to continue as more organic reference materials become available. Data evaluation for these studies includes the calculation of median values, mean values, standard deviations, coefficients of variation, mean errors, relative mean errors and % recoveries. In addition, paired sample plots are prepared and the results ranked by laboratory.

International studies

Under the auspices of the International Joint Commission and the Canada-US Great Lakes Water Agreement, 18 large multi-sample QC studies have been prepared at NWRI and distributed to more than 50 US and Canadian environmental laboratories in the Great Lakes Basin. These international studies are large. Typically each study includes ten to 15 test samples distributed to about 25 to 35 laboratories. Ten to 15 parameters are addressed per study.

The data interpretation for these studies is handled by computer with the performance and appraisals prepared by a seven member international data quality work group. The turnaround time for these program specific interlab studies is about six to 12 weeks. Each participant receives its own laboratory specific appraisal and an assessment of its performance relative to other laboratories. Managers of programs and the users of the data are involved. Access to the confidential lab appraisals is possible and indeed encouraged by having users consult the source of their data.

Other studies

Special QC studies are designed and conducted when the cause of analytical problems are not readily identified or when potential problems on analytical methods are suspected. These studies are also used to test the ruggedness of the methods and complement the interregional and national studies.

TABLE I: Research and Development of Certified Reference Materials at NWRI

Constituent Class	Code	Contaminant	Matrix	Status/yr	Certification	Remark
Organic	QAM-1	PCBs	lake sediment	RM, 79	—	wet (A)
	EC-1	PCBs	"	RM, 80	82	dried (B)
	EC-2	PCBs	"	RM, 81	*	dried (B)
	EC-3	chlorobenzenes	"	RM, 82	*	dried (B)
Inorganic	WQB-1	trace elements	"	RM, 81	*	dried (B)
	WQB-2	Hg	"	RM, 80	82-83	dried (B)
	WQB-3	As, Se	"	*	*	dried (B)
	several	major ions	waters	*	—	A and B
	several	trace elements	waters	*	—	A and B

A = spiked
B = natural contaminated
* = in progress

(a) Except for QAM-1 all sediments were freeze dried and are at −200 mesh.

(b) The major ions included about 12 constituents and are contained at unpreserved conditions (+4°C). The samples are in either distilled water or are natural waters.

(c) The trace metal samples (12 to 15 metals) are contained in either 0.2% (V/V) HNO_3 or 2% (V/V) HNO_3. The samples are either distilled water standards or spiked natural waters.

(d) The above materials represent the official materials undergoing certification. Augmenting this list are about 50 reference materials (waters, sediment and fish) that are in limited stock (200 litre units, 5 to 20 kg units) and are reserved for interlab quality assurance studies.

In addition to conventional quality control studies, we also conduct method specification studies to generate multi-operator, multi-laboratory specification statements (namely precision, accuracy and detection limit) for each analytical method used by the Water Quality Branch laboratories across Canada. These laboratories use specific methods to generate data which are stored in a national data bank. Specification statements, derived from round robin interlaboratory studies, are therefore indexes of reliability, credibility and the limitation of the data routinely generated by using the methods. These studies form an integral and essential part of the measurement and data interpretation process.

We also actively collaborate with international organizations such as the Association of Official Analytical Chemists and the American Society for Testing Materials in preparing interlaboratory studies for the generation of standardized methodologies.

Having discussed the various types of interlaboratory Quality Control studies in our quality assurance program, we shall now discuss the other key components (Figure 1).

Methods development

The quality of data generated depends firstly on the quality of the analytical method and secondly on how it is used for the analysis. Therefore, method development and validation are important components in an effective quality assurance program. Suitable analytical methods are provided to the routine laboratories for the generation of analytical data. A complete list of methods used by the regional laboratories can be found in the Analytical Methods Manual of the Inland Water Directorate, Environment Canada.[2]

Sample processing

Even when one uses a suitable and well validated analytical method to generate data, the data generated are only as good as the sampling program. For routine analysis and for interlaboratory quality control studies, the integrity of samples must be assessed. This is a prerequisite for reliable data and for the success of the interlaboratory program. Sample stability must be maintained in both cases.

Realizing the importance of sample integrity, investigations of sample stability and generation of sample storage and preservation procedures are accepted as an integral part of our quality assurance program.

A word of caution

So far, we have highlighted the key components of an effective laboratory quality assurance program and introduced our own program for environmental substrates and parameters. However, not all quality assurance studies are effective in assuring data quality. Quality assurance studies involving two or three laboratories are ineffective when valid CRM's are not incorporated into the studies. In reviewing other quality assurance studies, we have found a number of cases where they have failed to identify problems when serious problems did exist. An oversimplified quality assurance study can often lead to false confidence in data.

Reference standards

CRM's are stable, homogeneous and well-characterized reference materials prepared in quantity having essentially an identical or similar matrix to the field program materials. A similar matrix is necessary to eliminate or reduce the matrix effect between reference and test samples. RM's are similar to CRM's except they are less vigorously characterized. It requires a rigorous study of an RM before true values can be assigned to the various constituents. Only then does an RM become classed as a CRM.

Both CRM's and RM's are used in our quality control studies. They are also distributed to our regional laboratories to increase the effectiveness of their in-house quality control program. A list of the reference materials currently used in our quality assurance programs is provided in Table I.

The application of RM's and CRM's are numerous.[1,3] Interlaboratory programs that are not based on CRM's can only give a measure of between-laboratory precision, not accuracy. The need to identify both precision and accuracy in controlling a lab measurement system is well recognized. According to Hunter,[4] no measurement system can be truly under control without measures of both its precision and its interlaboratory bias (a reflection of accuracy).

References

1. Uriano, G.A. and Gravatt, C.G. The role of reference materials and reference methods in chemical analysis, in CRC Critical Reviews in analytical Chemistry, 361, 1977.
2. Analytical Methods Manual, Inland Water Directorate, Ottawa, Environment Canada, 1979.
3. Taylor, J.K., Anal. Chem., 53 (14), 1588A-1596A, 1981.
4. Hunter, J.S., Science, 210, 869-874, 1980.

INTRODUCTION

This report is a compilation of year-end study progress reports of the Analytical Methods Division for study year 1982/83. Each report provides the reader with a summary of the study, the significant findings and the name(s) of the investigator(s). Further details about any of the studies can be obtained by directly contacting the investigators. The reports are listed numerically to correspond to the order in the NWRI Directory of study forecasts.

J Lawrence

ANALYTICAL METHODS DIVISION

The mandate of the Analytical Methods Division is to advance knowledge, establish and maintain expertise and provide information on analytical chemistry and microbiology in support of Departmental programs. Providing information includes analytical methodology support to IWD analytical laboratories, NWRI scientists, the Great Lakes Water Quality Program, the Toxic Chemicals Management Program and other clients, and implementing interlaboratory quality assurance programs for regional, national, LRTAP, PPWB and GLWQP laboratories. In this respect, we can be considered a combined research division and national laboratory.

The division is organized into four sections, Analytical Chemistry Research, Quality Assurance and Methods, Microbiology Laboratories, and Computer Sciences.

Analytical Chemistry Research Section (ACRS)

The research and development work conducted within this section is devoted to the development of new techniques and improvement of existing techniques for the identification and measurement of the priority chemical contaminants of water, sediment and biological material. Emphasis is on the use of analytical techniques such as high pressure liquid chromatography, GC/MS, gas chromatography (packed column and wall coated open tubular capillary column) atomic spectroscopy and electrochemical techniques (ion-selective electrodes, kinetic potentiometry, coulometry, twin-cell linear potential sweep voltammetry and other polarographic techniques). 1982/83 was the first full year of operation for the Clean and Hazardous Chemicals Laboratory. All systems functioned according to specification and we are now able to undertake studies requiring this special facility.

Quality Assurance and Methods Section (QAMS)

The Quality Assurance and Methods Section is responsible for establishing quality assurance programs to monitor laboratory performance to ensure that data generated are valid and compatable on a regional, interagency, interdepartmental, national, and international basis. This also includes laboratories of the private sector engaged in contract work for Environment Canada, the International Joint Commission and the Federal Interdepartmental Committee on Pesticides in Water and Sediment. In addition to the design and implementation of these national and international quality control studies, other important activities include the development of standard environmental reference materials (water, sediment and biota) for various chemical parameters, interlaboratory calibration, the generation of interlaboratory specifications for precision, accuracy and detection limits and other related support to IWD analytical service programs.

The Section is also responsible for adapting, developing and providing suitable chemical methodologies for water, sediments and biota and to advise on, or solve, analytical problems encountered in client laboratories.

Microbiology Laboratories Section (MLS)

Microbiological Laboratories have two main program areas. One is to develop and evaluate microbiological methodologies and criteria for monitoring, assessing and maintaining water quality from the viewpoint of health hazards and eutrophication, including mutagens and toxicants. The other is environmental research related to the establishment of the extent of a waste's (sewage, industral waste, farm run-off) influence on water bodies, the rate of its degradation and the determination of the distribution of specific microorganisms and their roles in the aquatic ecosystem especially those under stress, such as from acid rain.

Computer Services Section (CSS)

The Computer Services Section is responsible for providing centralized computer facilities for all groups within CCIW. The section is essentially service oriented. It is responsible for the operation and maintenance of the computer on a daily basis, for planning and evaluating the future computing needs of the Centre and ensuring that adequate systems are available when needed.

ANALYTICAL METHODS DIVISION - Study Forecasts 1982/83

Project No.	Title	Leader
600	Analytical Methods Division Administration	J. Lawrence
601	GC/MS-Chemical Ionization Methodology for Environmental Analysis	F.I. Onuska
602	Quantitative Determination of PCB's in Sediments	F.I. Onuska
603	Determination of Metals in Environmental Samples by ICAP	P.D. Goulden
604	Determination of Non-metals in Vacuum Ultraviolet Range of ICAP	P.D. Goulden
605	Determination of Chromium in Water by Atomic Absorption Spectroscopy	P.D. Goulden
606	Electroanalytical Techniques in Water Analysis	I. Sekerka
607	Alternating Standard-Sample Technique in Water Analysis	I. Sekerka
608	Concentration, Analysis and Identification of Trace Analysis	B.K. Afghan
609	Method for Phthalate Esters by High Pressure Liquid Chromatography	B.K. Afghan
610	Consultation, Technology Transfer, Special Services, and Instrument Maintenance	B.K. Afghan
615	Methods Development and Confirmation of Contaminants in the GLB	F.I. Onuska
616	Radioimmunoassay Techniques for Dioxins	B.K. Afghan
619	Dioxins and Benzofurans Methodology	B.K. Afghan
621	Media, Wash-up, Instrument and General Support	R. McInnis
622	Legionella	B.J. Dutka
624	Effect of Acid Precipitation on Fungi in Fresh Water	J. Sherry
625	Microbial Nitrogen Cycle Methodology	B.J. Dutka

ANALYTICAL METHODS DIVISION - Study Forecasts 1982/83

Project No.	Title	Leader
626	Bacterial Toxicity Workshop	B.J. Dutka
628	Bacterial Water Quality Surveillance Lower Lakes	S.S. Rao
683	Acid Rain Effects on Microbial Response in Aquatic Ecosystems	S.S. Rao
641	Quality Assurance and Methods Section - Administration and Measurement	A.S.Y. Chau
642	FICP Quality Control Studies	A.S.Y. Chau
643	Interregional Quality Control Program: WQB Methods Manual	Chemist
644	Development of Standard Reference Materials and Reference Materials	V. Cheam
645	Method Adaptation for WQB Laboratories	V. Cheam
646	Method Developments for Herbicides	Chemist
653	LJC Quality Assurance Study	K.I. Aspila (Inorganic) A.S.Y. Chau (Organic)
654	Prairie Provinces Water Board Quality Assurance Program	Chemist
657	Interlaboratory Quality Assurance Program: TCMP	H.B. Lee
659	LRTAP Quality Assurance Program (Phase 1)	K.I. Aspila
670	Computer Services for Water Management Research	H.C. Pulley
681	Capital Equipment Acquisition (ACRS)	J. Lawrence
682	Capital Equipment Acquisition (QAMS)	J. Lawrence

ANALYTICAL METHODS DIVISION STAFF

Chief: Dr. John Lawrence

Secretary: Joyce Burford

Analytical Chemistry Research Section

Head, Dr. B.K. Afghan

Jim F. Ryan
Robert (Bob) J. Wilkinson

Dr. Peter D. Goulden
Donald H.J. Anthony

Dr. Ivan Sekerka
Josef (Joe) F. Lechner

Dr. F.I. Onuska
Ken Terry

Quality Assurance and Methods Section

Head, A.S.Y. Chau

Keijo I. Aspila
Dr. Ven F. Cheam
Dr. H.B. (Bill) Lee
Ms. Yvonne Stokker
Mrs. Susan Todd

Microbiology Laboratories Section

Head, B.J. Dutka

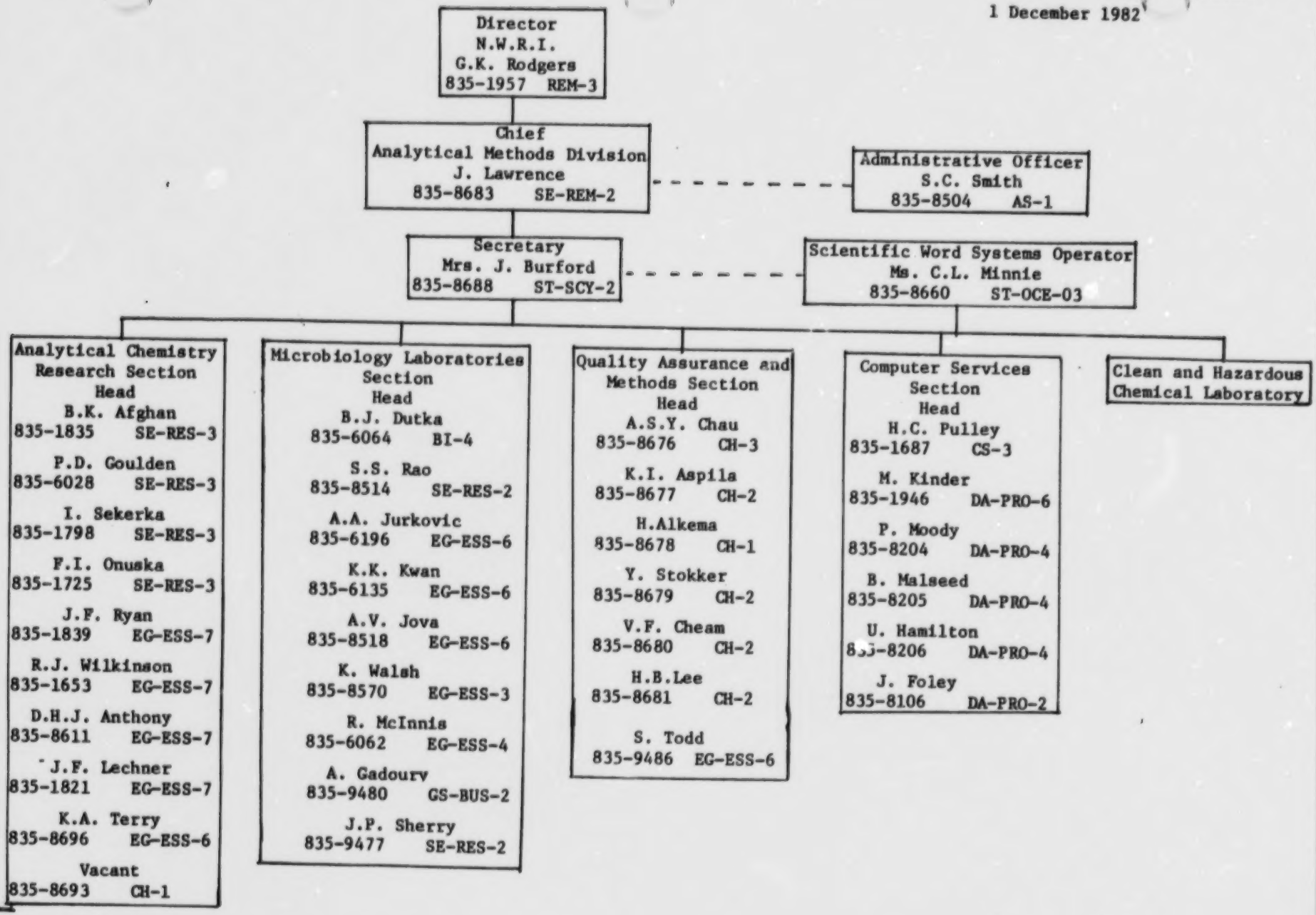
Dr. Salem Rao
Annette Gadoury
Arnold Jurkovic
Alfred Kwan
Audrey Jova
Rodney McInnis
Kathryn Walsh
Dr. Jim Sherry

Computer Services Section

Head, H.C. Pulley

Maureen Kinder
Millie Hamilton
Brent Malseed
Jackie Foley
Pat Moody

ANALYTICAL METH[illegible]DIVISION
1 December 1982



Analytical Chemistry Research Section

601: GC/MS CHARACTERIZATION OF TOXAPHENE IN ENVIRONMENTAL SAMPLES

by

F.I. Onuska and K. Terry

INTRODUCTION

The objectives of this study were to improve separation techniques for toxaphene and to refine or develop analytical methodology for characterization of toxaphene compcsition (confirmation) using chemical ionization gas chromatography-mass spectrometry at 500 ng/μL of toxaphene injected.

Research Results

HRGC/ECD analyses of toxaphene were performed with a Varian 6000 Vista gas chromatograph with an on-column capillary injection system and a standard Ni-63 ECD. For the chromatography we used WCOT columns. Our WCOT columns were 30 m x 0.2 mm i.d. O.V-1; 30 m x 0.2 mm i.d. OV-225 and 30 m x 0.2 mm SE-54 fused silica capillaries. Hydrogen was used as a carrier gas with a linear velocity of 35-45 cm/s. An initial temperature of 115°C was held for 1 min, after programmed to 170°C at 10°C/min and from 170° at 2°C/min to 220°C where it was held at final temperature for 10 minutes. The injector temperature was 115°C and after 1 minute programmed to 180°C at °C/min where it was held for 8 minutes. The detector temperature was 320°C. The detector makeup gas was nitrogen at a flow rate of 20 mL/min. To reduce the ECD dead volume, we inserted the WCOT column up to the detector source with the makeup gas introduced before the end of the column.

Gas chromatography - Chemical ionization mass spectrometry and GC/MS-electron impact study was performed on the Varian 311A GC/MS/DS system coupled directly to a Carlo Erba 4160 GC equipped with cool on-column injector.

Computerized GC/MS-EI does not provide sufficient data in toxaphene characterization and detection. Detection sensitivity was poor due to the excessive fragmentation of toxaphene under the electron impact conditions. Detection limit for GC/MS-EI full spectra is 2 μg injected. The toxaphene peaks eluting during temperature programming were scanned over the mass range of 80 to 550 in 2.3 seconds/decade. Data representing each spectrum was stored on disc. Up to 1200 scans were obtained for 1 chromatogram. The mass chromatograms constructed from the combined ion intensities of m/z 291 + 293 poorly resemble the peak envelope recorded from the TIC trace. GCpeaks in the TIC representing m/z 83 $[CHCl_2]^+$ ion eluted late, while GC peaks containing m/z 117 $[CCl_3]^+$ ion generally eluted earlier.

Examination of toxaphene by GC/MS-CI was examined by direct probe. The resulted spectra show multiple ion clusters. These ion clusters represented isomeric series of chlorinated camphenes having three typical empirical formulas, i.e.

$$C_{10}H_{(14-n)}Cl_n;\ C_{10}H_{(16-n)}Cl_n;\ C_{10}H_{(18-n)}Cl_n$$

Using HRGC/MS-CI revealed over 150 peaks. Various reactant gases were evaluated such as isobutane, methane and ammonia. It seems that isobutane and methane reactant gases are the best for toxaphene characterization but in negative ion CI ammonia produced mass spectra of toxaphene are very good.

Detection limit for the full readable mass spectra is 500 ng of toxaphane injected.

602A: AN EVALUATION OF SPLITLESS AND ON-COLUMN TECHNIQUES FOR THE DETERMINATION OF PRIORITY MICROPOLLUTANTS

by

F.I. Onuska, J.R. Kominar and K.A. Terry

INTRODUCTION

The superior qualitative information obtainable using WCOT columns has led to an increased demand for quantifying these multiresidue mixtures. The quantitative determination of complex mixtures is not reported, or only limited data is available. Much of what appears indicates the difficulty in achieving as high an accuracy and precision with WCOT columns as with packed columns. This problem is associated with the use of splitless vaporizing injectors. This observation has led many gas chromatographers to conclude that splitless injections are unlikely to find wide acceptance for the quantitative determination of broad boiling range samples.

In our laboratory, work on qualitative and quantitative determination of organic micropollutants such as chlorinated benzenes, polychlorinated biphenyls, toxaphene and other contaminants of environmental concern is in progress. This has led us to investigate the reliability of splitless and on-column injection techniques in high resolution gas chromatography.

Research Results

In view of this study, we recommend that analysts using splitless injection devices re-evaluate their quantitative methodologies. We have found that splitless injections can be used for some quantitative determinations, especially if an autosampler is used but their application for quantitation of multicomponent mixture at low picogram levels is by no means universal.

We have found on-column injectors much superior to splitless injections for quantitative analysis. It may be generalized that for wide boiling range mixtures, such as those often present in environmental samples, it is mandatory to use this technique in order to obtain reliable quantitative analytical data.

In the end, the analyst must choose an injection device and perform a critical evaluation using statistical methods to determine its suitability for a particular type of application.

This paper was presented at "International Symposium Capillary Chromatography '82" in Tarrytown, N.Y., October 5, 1982 and was submitted for publication to J. Chromatogr. Science.

References

1. K. Grob, K. Grob Jr. J. Chromatogr., 151 (1978) 311.

2. R.R. Freeman, T.A. Rooney, T.H. Przybylski, L.H. Altmayer, Hewlett-Packard Technical Paper No. 83, 1979.

602B: QUANTITATIVE DETERMINATION OF POLYCHLORINATED BIPHENYLS BY HIGH RESOLUTION GAS CHROMATOGRAPHY - ELECTRON CAPTURE DETECTION

by

F.I. Onuska, R.J. Kominar and K.A. Terry

INTRODUCTION

The most difficult task in the determination of multicomponent PCB residues is to identify individual isomers of the PCB mixture in the presence of such contaminants as chlordanes, DDT and its analogs, and toxaphene. We decided to develop a methodology which would solve these problems and would provide data for:

a) quantitation of individual isomers, important for toxicological studies and synergistic effect studies of various congeners in a particular PCB mixture in different matrices;

b) quantitation of characteristic groups (homologs) based on the number of chlorine atoms in the chlorinated biphenyl molecule, which can be used for long term degradation studies based on the individual capacity to interact with a matrix containing PCB;

c) determining total loading of PCB which would be more accurate and precise, since impurities would be subtracted from the chromatogram obtained.

Research Results

We have developed an integrated analytical methodology for PCB multiresidues in sediment samples that enables quantitation of PCB residues at levels as low as 0.1 µg/kg in sediments. PCB residues are characterized and quantified by WCOT column gas chromatography using electron capture detection (ECD). The peaks appearing in the chromatogram representing PCB congeners were identified by using a method of relative retention time matching. We used decachlorobiphenyl as the marker peak, and assigned a RRT of 1.000. Afterwards, we computed RRT values for PCB congeners as the ratio of the individual peak retention time to that of decachlorobiphenyl. Since not all congeners are commercially available, we used as many as 22 congeners for primary quantitation known that they represent approximately 47 percent of the total concentration of PCB congeners of 1:1:1 Aroclors 1242:1254:1260 mixture. These peaks out of the remaining 95 peaks present in a typical WCOT chromatogram contained the most useful information for describing the similarity among PCB and PCB like residues. Relative retention times (RRT) and relative response factors (RRF in area/pg) were first established for the 22 congeners in the standard calibration mixture. Afterwards, the remaining PCB peaks were grouped according to the number of chlorine atoms in the polychlorinated biphenyl molecule.

From the weight percent of each homolog group in Aroclors 1242, 1254 and 1260, we determined the weight of each homolog in a 600 or 900 pg/μL sample of 1:1:1 Aroclor mixture. From these homolog weights and respective integrated areas we subtracted the amounts and corresponding areas of the 22 congeners as related to our standard calibration mixture. Using the remaining integrated areas and weights for each homolog group average RRFs (area/pg) for the remaining homologs were determined.

By matching RRTs and using the averaged RRF data along with precise RRFs for the 22 congeners, we could calculate the amount of each PCB homolog group, and the total amount of all PCB in the sample and the amount of each of the 22 individual congeners.

Results were submitted for publication to the Journal of Chromatography.

References

1. K. Ballschmiter, M. Zell, Analysis of PCB by glass capillary gas chromatography. Fresenius Z. Anal. Chem., 1980 302, 20-31.

2. T.R. Schwartz, D.L. Stalling, J.D. Petty, J.W. Hogan, B.K. Marlow, R.D. Campbell, R.L. Little, Extended Abstract. A MUMPS (DSM-11) Derived Data Base for Congenera Specific PCB Analysis Leading to Pattern Recognition Studies. ACS-Meeting, Division of Environ. Chem., Kansas City, Missouri, Septmber 1982.

3. F.I. Onuska, J.R. Kominar and K. Terry. An Evaluation of Splitless and On-Column Injection Techniques for the Determination of Priority Micropollutants. Presented at "Capillary Chromatography '82 International Symposium" in Tarrytown, N.Y., October 5th, 1982. Submitted for publication to J. Chromatogr. Sci.

603: DETERMINATION OF METALS IN ENVIRONMENTAL SAMPLES BY ICAP

by

P.D. Goulden and D.H.J. Anthony

INTRODUCTION

The methodology that has previously been developed here for the analysis of environmental samples by ICAP uses an automated hydride-generation system for the simultaneous determination of As, Se, Sn, Sb and Bi (1) and a pneumatic nebulizer-heated spray chamber system for the determination of other trace metals and major ions (2).

The hydride-forming elements are determined with the acid and its concentration that is optimum for selenium, this is not the optimum for the other elements, particularly tin. With the increasing interest in determining very low levels of tin in environmental samples, there is a need for further work on the determination of tin, on possible intereferences and on sample preservation. It is believed that the heated spray chamber system used for adding liquid samples to the plasma can be improved by the use of ultrasonic nebulization. Preliminary studies have shown that it gives better sensitivity, less noise and smaller matrix effects.

Research Results

It has been shown that the optimum condition for stannane production is in a matrix of 0.2N HNO_3. This gives a sensitivity that is at least ten times greater than in the 4N HCl used when it is determined simultaneously with selenium. The nitric acid preservative used by WQB for trace metal preservation is satisfactory for tin.

Studies have been made on the parameters affecting the efficiency and stability of ultrasonic nebulizer system. The critical factor in the drying-desolution step is to prevent the fine aerosol produced by the nebulizer from agglomenating before it can be dried and stabilized. Equipment to carry out this process has been designed and built.

The improvement in detection limit with this system is a factor of about five over that using the pneumatic nebulizer, heated spray chamber. Most of this work has used the commercially-available transducers which are mounted on glass discs. A variety of ways of assembling these discs has been tried to determine the best configuration for our use. These transducers operate at a frequency of 1.4 MHz at a power of up to 60 watts. Work with other transducers (which are only available unmounted) indicate that a frequency of 3.2 MHz is likely to produce better results, and also that a larger transducer is desirable. The supply of such transducers is still being investigated.

References

1. Goulden, P.D. and D.H.J. Anthony, Anal. Chem., 1981. 53, 2027-2029.

2. Goulden, P.D. and D.H.J. Anthony, Anal. Chem., 1982. 54, 1678-1681.

605: DETERMINATION OF CHROMIUM IN WATER BY ATOMIC ABSORPTION SPECTROSCOPY

by

P.D. Goulden and D.H.J. Anthony

INTRODUCTION

The determination of chromium in natural waters is commonly carried out by oxidizing the chromium to Cr^{VI} and extracting this CrVI with a solvent and a chelating agent such as ammonium pyrollidine dithiocarbamate (APPC). The solvent extract is then examined via atomic absorption spectroscopy. The procedure used in the Water Quality Branch (1) was bromine as the oxidizing agent. Reports from the regional laboratories of the WQB show that the procedure does not give consistent results, particularly in waters high in organics. This project was undertaken because of the direct request by the Yukon and Pacific Regional Laboratory for us to investigate the chromium methodology.

Research Results

It was shown that the problems experienced in the chromium analysis were due to incomplete oxidation of the chromium in Cr^{VI}. Bromine will not complete the oxidation in the presence of 'natural' organics, if Cr^{VI} is added to many natural waters the organics present will rapidly reduce it. It was found that a good oxidizing procedure was one that used potassium persulfate. This oxidizes the chromium, destroys the organics and can be thermally decomposed after the oxidation is complete (2).

A report describing this work has been written (3).

References

1. Analytical Methods Manual (1979). Environment Canada, Inland Waters Directorate, Water Quality Branch, Ottawa, Canada.

2. Goulden, P.D. and D.H.J. Anthony, Anal. Chem., 1978. 50, 953-958.

3. Goulden, P.D. and D.H.J. Anthony, "A modified method for the determination of chromium in natural waters". AMD Internal Report No. 59-AMD-3-82-PDG.

606: ELECTROANALYTICAL TECHNIQUES IN WATER ANALYSIS

by

I. Sekerka and J.F. Lechner

The method involves adsorption of organohalides from natural water samples on porous polymer Tenax GC followed by thermal desorption at 400°C and oxidative combustion to hydrogen halides. The halides are captured in water solution containing formaldehyde and sulfamic acid and measured either by direct potentiometry with high sensitive chloride ion selective electrode or by potentiometric titration with Hg^{2+} titrant solution. The efficiencies of the adsorption, combustion and detection as well as elimination of interferences are presented. Analysis time after adsorption is rapid (2 min) and procedures are simple, making the technique suitable for routine application.

INTRODUCTION

Halogenated organocompounds are of considerable interest in the environmental field research because they are suspected to cause adverse health problems[1,2]. Their presence and origin are well documented[3-9]. Current methods of analysis identify groups of organohalides such as volatile[9,10] and non-polar compounds. Recently the analysis for total organohalides as a group parameter has been recognized as an indicator of water quality because it includes in the measurement the amount of potentially harmful compounds[12,13]. The first step in the analysis for trace organohlaides in water is their separation and preconcentration. Several methods have been reported using the adsorption of organic compounds onto ground, granular activated carbon[14-16]. Another method is the mini-column method employing Amberlite XAD resin as the sorbent[13]. Solvent extraction has also been suggested for the separation and preconcentration step[17]. The efficiencies of liquid-liquid extraction, carbon and XAD resin have been evaluated by Janarden *et al.*[18-19] and by Chriswell *et al.*[20]. The extraction of trace amounts of organic compounds from water has been reviewed by Dressler[21]. Published data seem to favour the extraction with porous organic polymers over the other techniques.

The second step involved in the method is the desorption of the compounds from the sorbent. This can be performed either with a liquid or by heating. Liquid desorption with a number of elements has been applied mostly in combination with chromatographic detection of organic compounds[22]. In desorption, the compounds are released by the action of heat and these are transported by the carrier gas into the converter and/or detector. The desorption temperature must be high enough to allow all compounds of interest to be tranferred into the gaseous phase. The maximal desorption temperature is determined by the thermal stability of the sorbent. Tenax GC porous polymer was found to be stable up to 400°C whereas Amberlite XAD-2 was acceptable

to 275°C only[22]. The drawback of activated carbon is that due to the high desorption temperature some inorganic halides are detected and the column cartridges have to be treated by nitrate wash to displace inorganic chloride. Since the freshly ground activated carbon contains some halogens that are not removable a blank determination is necessary[23].

The third step of the total organohalides analysis is their conversion into a measurable form. The pyrolytic conversion of organohalides to simple halides has been reviewed by Debal and Levy[24]. Further development resulted in relatively standard procedure in which the sample is vapourized in the stream of an inert carrier gas and is joined by oxygen in a combustion zone held over 800°C. The resulting gases are swept into a detecting system.

The last step is the detection of halides. Generally, potentiometric or coulometric techniques in different variations have been applied. Kriggsman et al.[27] have described a semi-automatic argentometric preselected end-potential titration monitored by an Ag_2S ion-selective electrode. Potman and Sahmen[28] modified this method by using Hg^{2+} as titrant. The microcoulometric method based on argentometry has been described[12,25].

Based on the above information, the Tenax GC resin as the sorbent, thermal desorption in the carrier gas stream, combustion in oxygen rich atmosphere and direct potentiometric detection were selected, tested and optimized.

Experimental

Apparatus

Resin cartridges made of quartz with quartz fibre filter plugs on both ends were packed with Tenax GC 35/60 mesh (Enka, N.V., Holland) and heated to 400°C in the stream of CO_2 gas for 20 min to remove eventual contaminants. A Dohrman MO S-200 pyrolysis furnace with three independently heated zones was used for the oxidative combustion. The furnace was equipped with a quartz combustion tube connected to a water-cooled adsorption vessel. The water-cooled adsorption vessel was equipped with a combination high sensitive chloride ion-selective electrode[29]. The gases from the combustion tube were absorbed in 5 mL of the adsorption solution. The electrode exhibited practical detection limit of 20 ppb Cl^-. The detection limit of the system depends on the volume of the sample passed through the Tenax cartridge. Assuming a 1000 mL sample and 5.0 mL volume of the adsorbing solution, the detection limit is 0.1 ppb Cl^-.

Procedure

The water sample is passed through the resin cartridge at the rate of 10 mL/min. After the desired volume of sample is eluted, most of the residual water is removed in the stream of CO_2 (30 min) and the cartridge is inserted into the desorption inlet zone of the furnace heated to 400°C. Released and vapourized organics are swept by a continuous stream of CO_2 (100 mL/min) into a combusting zone held at 850°C where they are combusted in oxygen enriched atmosphere (100 mL/min). The gases then flow into the adsorption vessel where the halides are captured and determined. After the potential of the chloride-ion electrode reaches stable reading, the concentration of halide ions is determined by comparing with a previously prepared calibration graph. Alternatively, a preselected end-point titration system automatically balances the changes of potential by adding the Hg^{2+} titrant solution and the concentration of halides is calculated from the volume of added solution.

The efficiency of adsorption and thermal desorption (total efficiency) was established by analyzing the synthetic samples of water containing known amounts of organohalides. Recoveries of ten model compounds as shown in Table II averaged 80% at 1.0 ppb levels of chlorine or bromine in the sample. Relative standard deviations were in the range of 5% at 1.0 ppb levels.

Interferences

In a given system, the organosulfur and organonitrogen compounds are interfering substances. Their oxidative combustion produces ionic compounds (SO_3^{2-}, S^{2-}, NO_x, CN^-) which interfere with the response of chloride electrode as well as with mercurimetric titration. To eliminate this interference the adsorption solution contains formaldehyde (1 mL of 38% solution) and 0.1 g of sulfamic acid in 100 mL of water[30]. This solution eliminates the interference, and adjusts the pH and total ionic strength required for optimal performance of the electrode. Table I shows the results of the determination of carbontetrachloride in the presence of sulfur (carbondisulfide) a nitrogen (cyclohexylamine). No significant interference was observed.

One of the problems in organohalides analysis is to ensure that inorganic halides do not interfere. Data of the determination of carbontetrchloride in the presence of inorganic chloride as presented in Table IV show insignificant interference. Free chlorine present in disinfected water interferes and has to be reduced prior to the analysis.

Five, three-litre Lake Ontario water samples were taken for analysis by proposed method. Samples were divided into three, one-litre aliquots. The first aliquot was analyzed for organohalides without any treatment, whereas aliquots two and three were spiked with

a known amount of trichloromethane prior to the analysis. Results are summarized in Table II.

Conclusion

Analytical procedures involved are simple and rapid. The required instrumentation is realtively inexpensive and easy to operate. The interferences are eliminated. The sensitivity, recovery and precision compare well with other techniques. The described method is suitable for routine analysis of Tenax adsorbable organohalides in natural water. Proper selection of the sample volume allows the application of the method over wide range of concentration.

TABLE I. Influence of nitrogen and sulfur on chlorine determination

S Taken (μg)	N Taken (μg)	Cl Taken (μg)	Cl Found (μg)	Recovery (%)
		1.2	1.0	83
		12.0	11.0	92
1.4	1.7		0.1	
14.0	17.0		0.1	
1.4	1.7	1.2	1.1	92
14.0	17.0	1.2	1.3	108
1.4	1.7	12.0	12.5	104
14.0	17.0	12.0	12.9	108

Table II. Determination of organochlorine in lake-water

Sample No.	Cl Taken (μg/L)	Cl Found (μg/L)	Recovery (%)
1	0.0	68.0	-
	13.0	75.0	93
	130.0	187.0	94
2	0.0	27.0	-
	13.0	35.0	88
	26.0	48.0	91
3	0.0	41.0	-
	13.0	50.0	93
	65.0	91.0	86
4	0.0	52.0	-
	26.0	61.0	78
	130.0	159.0	87
5	0.0	91.0	-
	52.0	129.0	90
	130.0	191.0	86

REFERENCES

1. Drinking Water and Health (Recommendation of the National Academy of Sciences), Federal Register, 42, p 35764 (1977).

2. D.T. Williams, R. Otson and P.D. Bothwell in B.G. Afghan and D. Mackay, Eds. (New York: Plenum Press, 1980) pp 503-512.

3. J.M. Symons, T.A. Bellar, J.K. Carswell, J. DeMarco, K.L Kropp, G.G. Robeck, D.R. Seeger, C.J. Slocum, B.L. Smith and A.A. Stevens, JAWWA, 7, 634 (1975).

4. J.J. Rook, Water Treat. Exam., 23,234 (1974).

5. J.J. Rook, JAWWA, 68, 168 (1976).

6. S.A. Hubbs, J.S. Zogorski, D.A. Wilding, N.A. Ambuele, G.S. Allgeier and R.L. Mullins in R.L. Jolley, H. Gorchev and D.H. Hamilton, Eds. (Ann Arbor, Science Publishers, 1977) vol. 2, pp 605-611.

7. B.G. Oliver, Can. Res., 11, 21 (1978).

8. B.G. Oliver and J. Lawrence, JAWWA, 71, 161 (1979).

9. T. Bellar and J. Lichtenberg, JAWWA, 66, 734 (1974).

10. K. Grob and F. Zurcher, J. Chromatogr., 117, 285 (1976).

11. R.C. Dressman and A. Stevens, JAWWA, 71, 392 (1978).

12. R.C. Dressman, B.A. Najar and R. Redzikowski, J. Am. Water Works Assoc. Technology Conf. Proceedings, 3A-5 (1977).

13. W. Glaze, G. Peyton and R. Rawley, ES&T, 11, 685 (1977).

14. W. Kuhn, H. Sontheimer, Vom Wasser, 15, 65 (1973).

15. W. Wuhn, H. Sontheimer, Vom Wasser, 41, 1 (1975).

16. R.C. Dressman, E.F. McFarren and J.M. Symons, AWWA Technology Proceedings, AWWA Denver (1977).

17. R. Wegman and P. Greve, The Science of Total Environment, 7, 235 (1977).

18. K.G. Janardan, D.J. Schaeffer and S.M. Somani, Bull. Environ. Contam. Toxicol., 24, 154 (1980).

19. K.G. Janardan and D.J. Schaeffer, Anal. Chem., 51, 1024 (1979).

20. C.D. Chriswell, R.L. Ericson, G.A. Junk, K.W. Lee, Z.S. Fritz and H.J. Svec, JAWWA, 69, 669 (1977).

21. M. Dressler, J. Chromatogr., 165, 167 (1979).

22. W.E. May, S.N. Chesler, S.P. Cram, B.H. Gump, H.S. Hertz, D.P. Enagonio and S.M. Syszel, J. Chromatogr. Sci., 13, 40 (1975).

23. M.R. Jebel and P.V. Roberts, ES&T, 14, 970 (1980).

24. E. Debal and R. Lévy, Microchim. Acta, 2, 272 (1964).

25. D.M. Coulson and L.A. Cavanagh, Anal. Chem., 32, 1245 (1980).

26. W. Ladrack, F. Van De Craats and P. Gouverneur, Anal. Chim. Acta, 50, 219 (1970).

27. W. Krijgsman, B. Grieping, J.F. Mansveld and W.J. Van Ort, Microchim. Acta, 795 (1970).

28. W. Potman and E.A.M.F. Dahmen, Microchim. Acta, 303 (1972).

29. J.F. Lechner and I. Sekerka, J. Electroanal. Chem., 57, 317 (1974).

30. D.D. Perrin, Masking and Demasking of Chemical Reactions. (Wiley-Interscience, New York, 1970)), Chap. 3., p 45.

607: ALTERNATING STANDARD - SAMPLE TECHNIQUE IN WATER ANALYSIS

by

I. Sekerka and J.F. Lechner

In water quality characterization and management, bottle sampling and laboratory analysis are not satisfactory for extensive survey and profiling operations. A technique capable of "in-situ" measurement of the profile of the water body is of great importance. The technique based on the dynamic nonequilibrium response of the sensors has been developed. In this technique the sensors are exposed alternatively to standard and sample solutions for programmable time period, (the fastest frequency being 0.1 s) in a flow-through cell at 2 m/s flow rate. The differential of the standard and sample peaks are related to the parameter of interest. An immersible, microprocessor based digital system suitable for "in situ" measurement of dissolved oxygen, conductivity, pH and temperature is described. The sampling rate of 0.5 s for all three parameters allows to measure the changes within 1 m layer of water body at the immersing speed of 0.5 m/s. The theoretical aspects of the technique as well as the data logging and data handling system is described.

INTRODUCTION

In water quality characterisation, the analysis for dissolved oxygen (D.O.) is extremely important. D.O. levels in water are dependent on the physical, chemical, biochemical, and biological activities occurring in the water body; therefore, the D.O. is used as a primary indicator in pollution abatement and is a vital parameter in waste water treatment. D.O. measurements are often deceptively easy, but they can be extremely difficult when high accuracy and speed are involved. Great care is required in collecting water samples. The sample must not remain in contact with air, nor be agitated. Samples from any depth of natural water or from boiler water need special precautions to eliminate changes in pressure and temperature. The time lag between sampling and performing the analysis is of great significance. Errors and difficulties associated with the sampling can be minimized by analyzing for D.O. "in situ". Such measurements provide a more realistic value of oxygen distribution in natural water.

The need for a profiling device stems from the following requirements:

a) to improve the accuracy, reliability and efficiency of oxygen surveys;
b) to avoid errors inherent in the bottle sampling and laboratory analysis;
c) to increase the detail in any given profile;

d) to increase the precision of layer thickness and depth measurements which define zones of different D.O. concentration;
e) to reduce time, mean power and operational cost of survey work.

The following specifications for a profiler were set down as the target: to measure D.O., conductivity, temperature at the time constant of 0.5 s for all three parameters in the temperature range from 0 m to 25°C and from 0 to 500 m of depth. The accuracy and precision of ±0.1 ppm D.O., ±0.1°C and ±10 μS were required. Presently available voltammetric membrane D.O. sensors are based on steady state measurements[1]. Their main limitations have been due to the lack of long term stability, low sensitivity and, most importantly, slow response to changes in D.O. concentration. Based on our previous studies of the response time of electrochemical sensors[2], there are no D.O. and conductivity sensors fulfilling the demand of 0.5 s time response to the changes of D.O. or conductivity in existence. This has resulted in the development of the dynamic mode system of the sensors operation.

Experimental

Sensors assembly

A combination flow through cell made of Teflon contains all three sensors (D.O., temperature and conductivity) and is illustrated in Fig. 1.

Oxygen sensor is a nonmembrane amperometric type with Pt ring electrode potentiostatically polarized to -0.5 V vs. the SCE[3] using PAR 173 potentiostat. Two platinum rings covered with Pt-black form the conductivity sensor. An YSI 500 hypodermic thermistor probe measures the temperature. The calibration of the D.O. sensor was done using the standard Winkler titration method.

Testing apparatus

The apparatus for laboratory testing of the sensors (Fig. 2) consists of the sample and standard solution reservoirs, programmable three way valve (XANADU Programmable Timer and Alfa solenoid valve) sensor assembly (home-made) and a Saturn Teflon pump. The values of

the temperature, conductivity and D.O. concentration in both reservoirs are adjustable. The standard solution of 15 ppm D.O., 500 µS conductivity and 25°C was found to be most practical in respect of its preparation and maintaining during the field or ship operation. The programmable valve alternates the flow of the standard and sample solution through the sensors assembly in preselected intervals. The velocity of the flow is governed by a variable speed pump. Individual sensors are connected to appropriate meters (Keithley 602 electrometer, YSI MO32 conductance meter and YSI Tele-thermometer). The signals are registered by a Gould MO 2400 high speed recorder.

Field assembly

The design of the system suitable for in situ operation is shown in Figs. 3 and 4.

It consists of an immersible sonde and a deck unit. The immersible part (the sonde) comprises the standard solution reservoir, valve, sensors assembly, pump, meters and other electronics. It is connected via a cable to the surface unit which provides commands for the operation of the sonde, processes and stores the signals. The data are obtained in the graphical form and are also stored for further evaluation and interpretation.

Principle of operation

The standard solution is kept at constant condition of 25°C, 500 µS and 15 ppm of D.O. By the programmable action of the valve and the pump, the sensors are alternatively exposed to the standard and sample solution at preselected frequency. The signals of the sensors are being continuously monitored. Resulting record consists of the set of peaks, the peaks of standard representing the baseline. The height of the sample peaks (Δ) is related to the parameter of interest and the calibration curves of all three parameters are constructed. The higher the peaks, the lower the temperature, conductivity and D.O. of the sample. In other words, the sensors are operated in a non-equilibrium dynamic mode without waiting for a steady-state reading.

Results and Discussion

The responses of all three sensors were found to be linear and simple calibration graphs can be constructed as well as simple mathematical equation can be applied for the computer programme. Increasing speed of the standard-sample alternation gave usable results down to 0.1 s per peak for all three sensors involved. Optimal speed was found to be 0.25 s per peak. In given geometry of the flow-through cell, the optimal flow rate was 2 m/s.

Fig. 2 Laboratory test apparatus

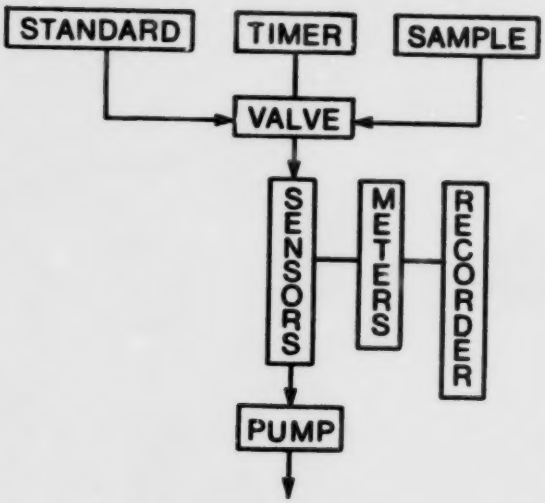


Fig. 3 Block diagram of the sone

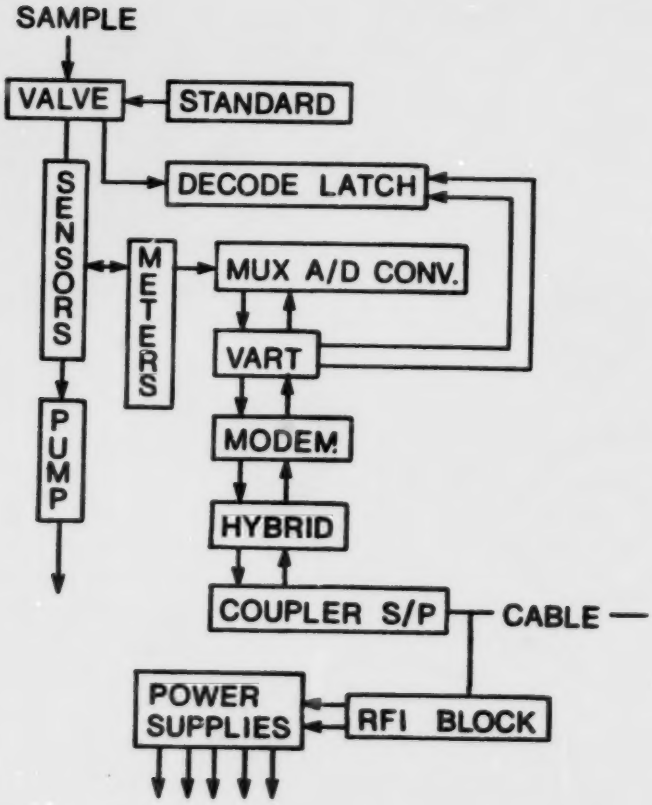
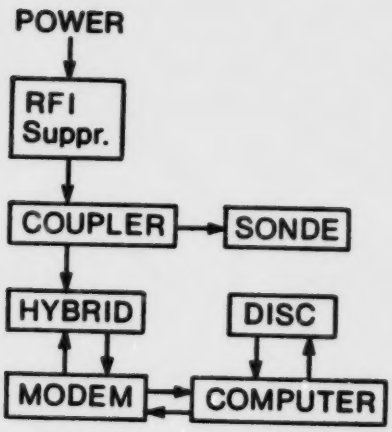


Fig. 4 Block diagram of the deck unit



The response of the conductivity sensor is affected by the changes of the sample temperature by a factor of 2% per 1°C. The microcomputer programme includes the equation correcting the conductivity values to 25°C. Varying temperature and conductivity of the sample are registered by the D.O. sensor as apparent changes of D.O. concentration. The correction factors of 0.1% per 1 μS and 0.5% per 1°C were experimentally established and the actual concentration of the D.O. was calculated by the computer according to the following equation:

$$D.O. = D.O._{ST} - R_o f_o \left(1 - \frac{dt\ c_{ot}}{100}\right) \left(1 - \frac{dC\ c_{oc}}{100}\right) \qquad (1)$$

where D.O. is dissolved oxygen in ppm, $D.O._{ST}$ is dissolved oxygen of the standard solution, R_o is the reading (peak height in mm), f_o is the calibration factor (ppm/mm), dt is the difference of the standard-sample temperature, c_{ot} is the temperature coefficient, dC is the difference of the standard-sample conductivities and c_{oc} is the conductivity coefficient.

Surfactants, sulfite and sulfide ions are potential interferences for the D.O. sensor. No interfering effect of surfactants and sulfite was observed either in respect to changes in the response or due to poisoning of the D.O. or conductivity sensor. The presence of H_2S is registered as apparent D.O. but in natural water under normal circumtances, D.O. and H_2S do not coexist. During six months of six-hour daily operation using Lake Ontario water, no significant changes of the sensors' performance were observed. The required maintenance procedure was weakly mechanical cleaning of the sensors and recalibration. The performance data of the system are summarized in Table 1.

TABLE 1. Performance of the system

D.O. (ppm)			Conducitivity (μS)			Temperature (°C)		
Winkler	Dynamic Mean (n=5)	S_r (%)	Cell	Dynamic Mean (n=5)	S_r (%)	Hg Meter	Dynamic Mean (n=5)	S_r (%)
15.2	15.1	3	401	405	2.0	25	25.1	1.5
10.1	10.0	4	345	344	2.0	20	19.8	2.0
5.3	5.1	3	312	310	1.8	15	14.9	1.2
2.1	1.9	5	285	287	1.5	10	10.2	1.1
1.2	1.0	9	261	265	1.0	5	5.1	1.5
0.5	0.4	8	228	231	3.0	2	2.1	2.0
0.1	0.15	20	169	171	4.0			

The profiling system described here gave satisfactory performance for monitoring sudden changes of all three parameters under laboratory conditions. The practical field application of the computerized system is scheduled for the summer 1983.

References

1. L.C. Clark, Am. Soc. Art. Int. Org., 2, 41 (1956).

2. I. Sekerka and J.F. Lechner, (in press).

3. Ch. M. Wolff and H.A. Mottola, Anal. Chem. 49, 2118 (1977).

608: CONCENTRATION, ANALYSIS AND IDENTIFICATION OF TRACE ORGANICS

by

B.K. Afghan, J.F. Ryan and R.J. Wilkinson

INTRODUCTION

Due to increasing concern of large number of chemicals entering in aquatic environment, there is a need to develop appropriate analytical techniques for detecting analysis and confirming these chemicals at ultra-trace levels. In our laboratory, the use of high pressure liquid chromatography-multidetection system and/or other spectroscopic techniques have been exploited for trace and ultra trace analysis.

This report will present a summary of the work carried out during FY 82/83 with special reference to AMI scanner, chlorophyll and phenols using the above techniques.

Automated Multiwavelength Identification Scanner

This scanner was developed as an accessory to spectrofluorescence spectrophoto meter to achieve wavelength programming, obtain a synchronous fluorescence spectra and run excitation/emision spectra. The accessory is microprocessor controlled and does carry out these functions on semi-automated basis. Scan rates, time and wavelength programming capabilities can be changed to suit a particular analysis. This accessory together with fluorcence spectrophotometer was also interfaced with high pressure liquid chromatography to provide an excellent means of carrying out quantitative and confirmational analysis. This system has been utilized to determine polynuclear aromatic hydrocarbons[1], carbamates[2] and chlorophyll pigments[3].

The AMI Scanner was also compared with commercial instrument and was found to be cost-effective. The AMI scanner can also be used with any fluorescence spectrophotometer to carryout the above functions. Typical results are shown in Figures 1 and 2 which show the wavelength programming and scanning capabilities of the system.

Chlorophyll

This work was initiatied to satisfy the needs of various laboratories within IWD. The main goals of the activity was to develop an improved method for analysis of chlorophyll pigments as well as develop a preparative scheme whereby one can isolate, purify the individual pigments and store the resultant pigment for use as a standard.

Work to date involved reevaluation of various extraction techniques together with the study of chlorophyll chemistry to devise an improved method for preservation of the extracted chlorophyll from the samples. It was observed that the light as well as heavy metal catalysis were the main causes for unstable nature of the chlorophyll in solution. An appropriate technique was developed to minimize the degradation of chlorophyll pigments with special reference to chlorophyll a. A five gear stability data for chlorophyll is also available. Figures 3 and 4 show the effect metal catalized hydrolysis and photolysis of chlorophyll a respectively.

Number of techniques for analysis of chlorophyll pigments were evaluated. These included spectrophotometry, fluorescence and HPLC with absorptiometric and fluorescence detection. HPLC with absorptiometric and/or fluorescence detection offer an improved means of determining chlorophyll pigments.

HPLC can also be used on a preparative scale to isolate and purify individual chlorophyll pigments.

Phenols

Various methods for extraction of phenols in environmental samples and related materials were evaluated. Extraction with trisodium phosphate was found to be superior for aqueous samples, sediments, commercial chlorophenol formulations and wood preservatives. This extraction technique gave low recoveries for wood shavings due to coprecipitation of phenols with humic acid/fulvic acid type of material. Extraction in acetonitrile or methanol using polytron homogenizer and/or emicator provided the quantitative extraction.

A preparative HPLC system utilizing styragel GPC column was used as an initial step for cleanup. An appropriate function containing phenols were analyzed by spectrophotometric, spectrofluormetric, HPLC or gas chromatography.

References

1. B.K. Afghan and R.J. Wilkinson, "Method for Determination of Polynuclear Aromatic Hydrocarbons in Environmental Samples" - Unpublished report 20-AMD-3-81-BKA, available from Analytical Methods Division, National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, Canada.

2. B.K. Afghan and J.F. Ryan, "Method for Determination of Carbamate Pesticides in Environment Samples" - Unpublished Report 60-AMD-3-82-BKA, available from Analytical Methods Division, National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, Canada.

3. B.K. Afghan and J.F. Ryan, "Improved Method for Isolation and Determination of Chlorophyll Pigments" - in preparation for publication.

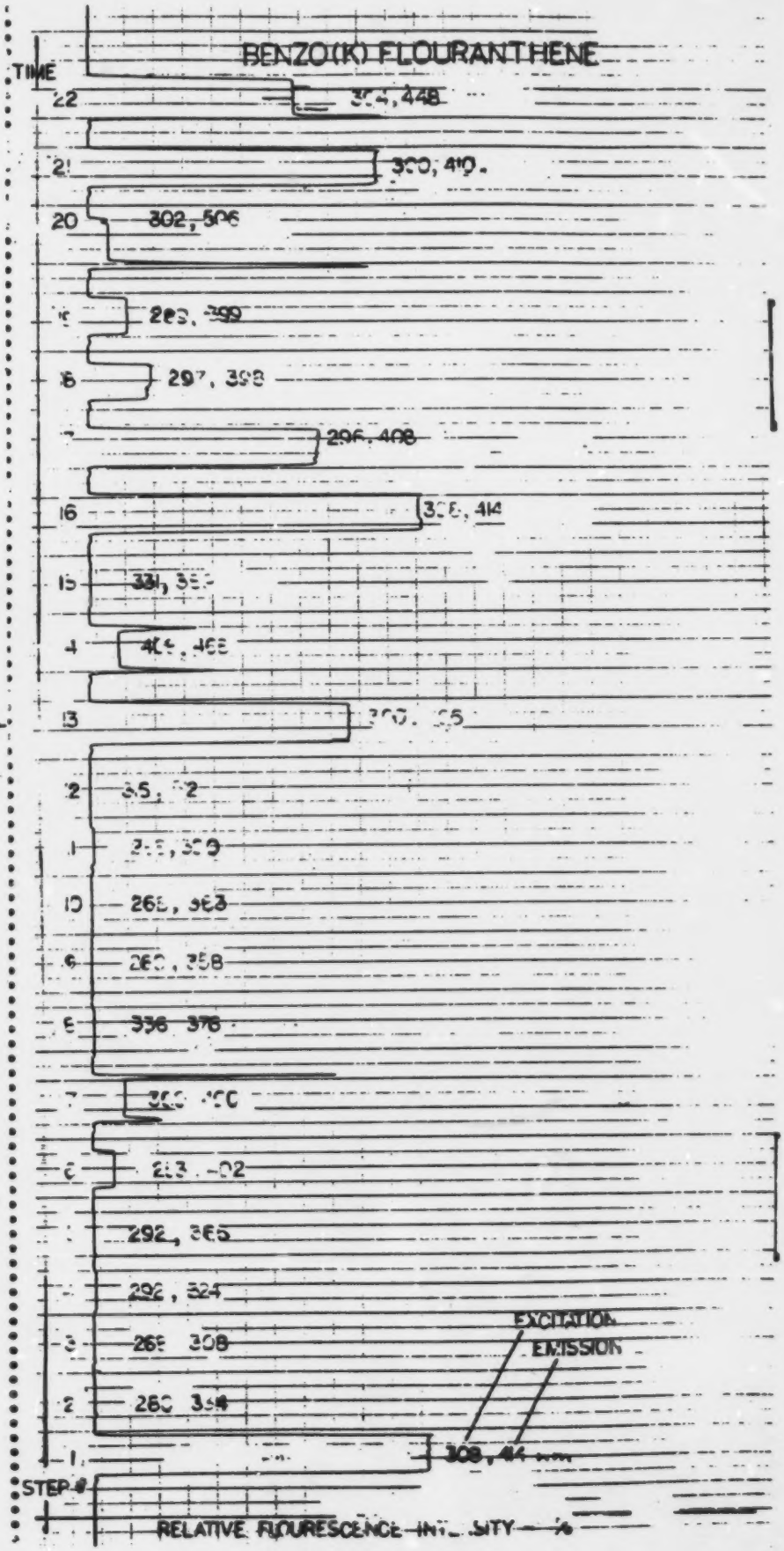

BENZO(K) FLOURANTHENE
TIME
22
21
300, 410
20
302, 506
16
15
331, 3
4
13
2
1
10
9
8
7
6
5
4
3
2
1
EXCITATION
EMISSION
STEP #
RELATIVE FLOURESCENCE INTENSITY

Figure 1.

SPECTRUM OF CHRYSENE

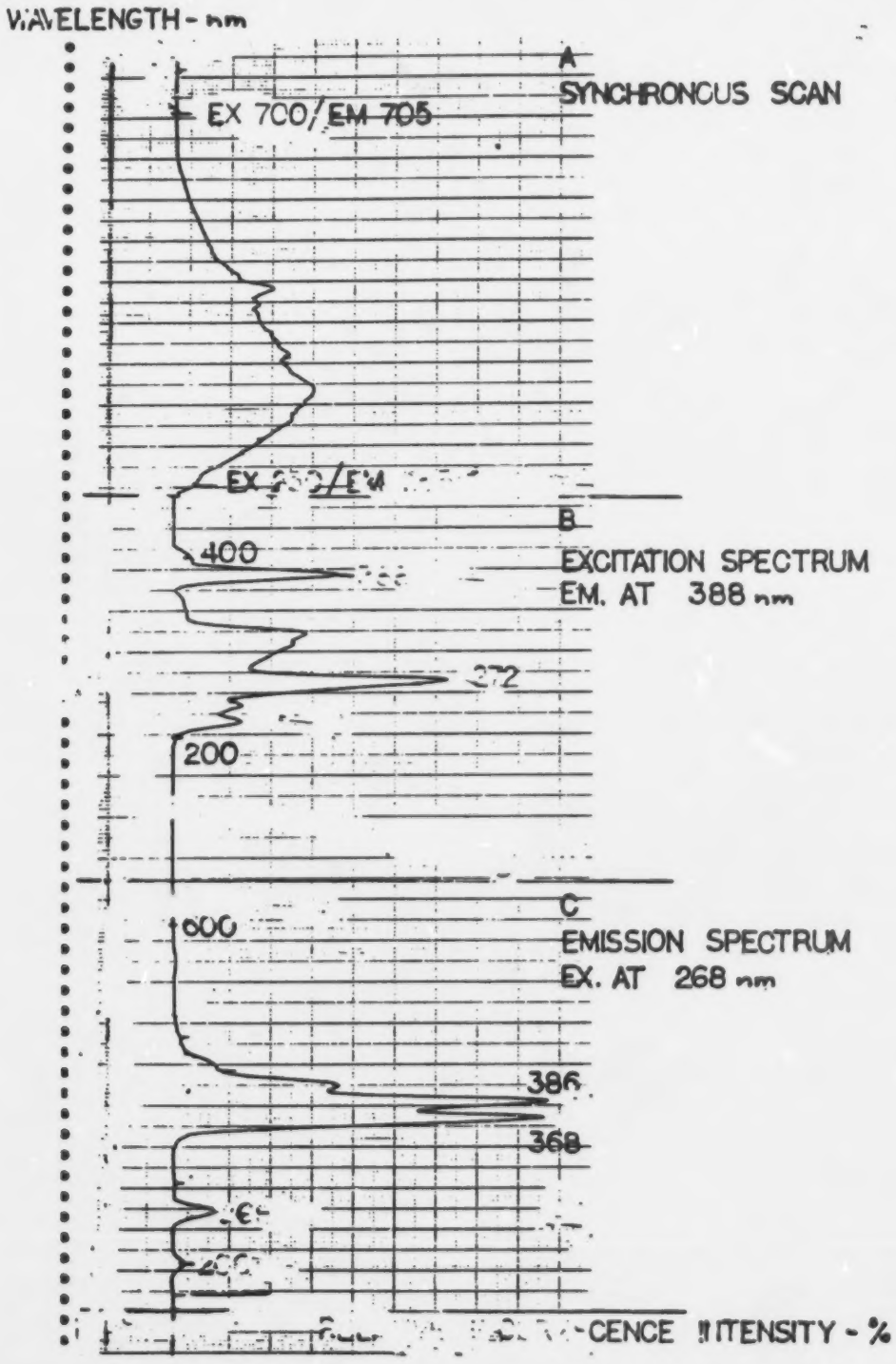


Figure 2

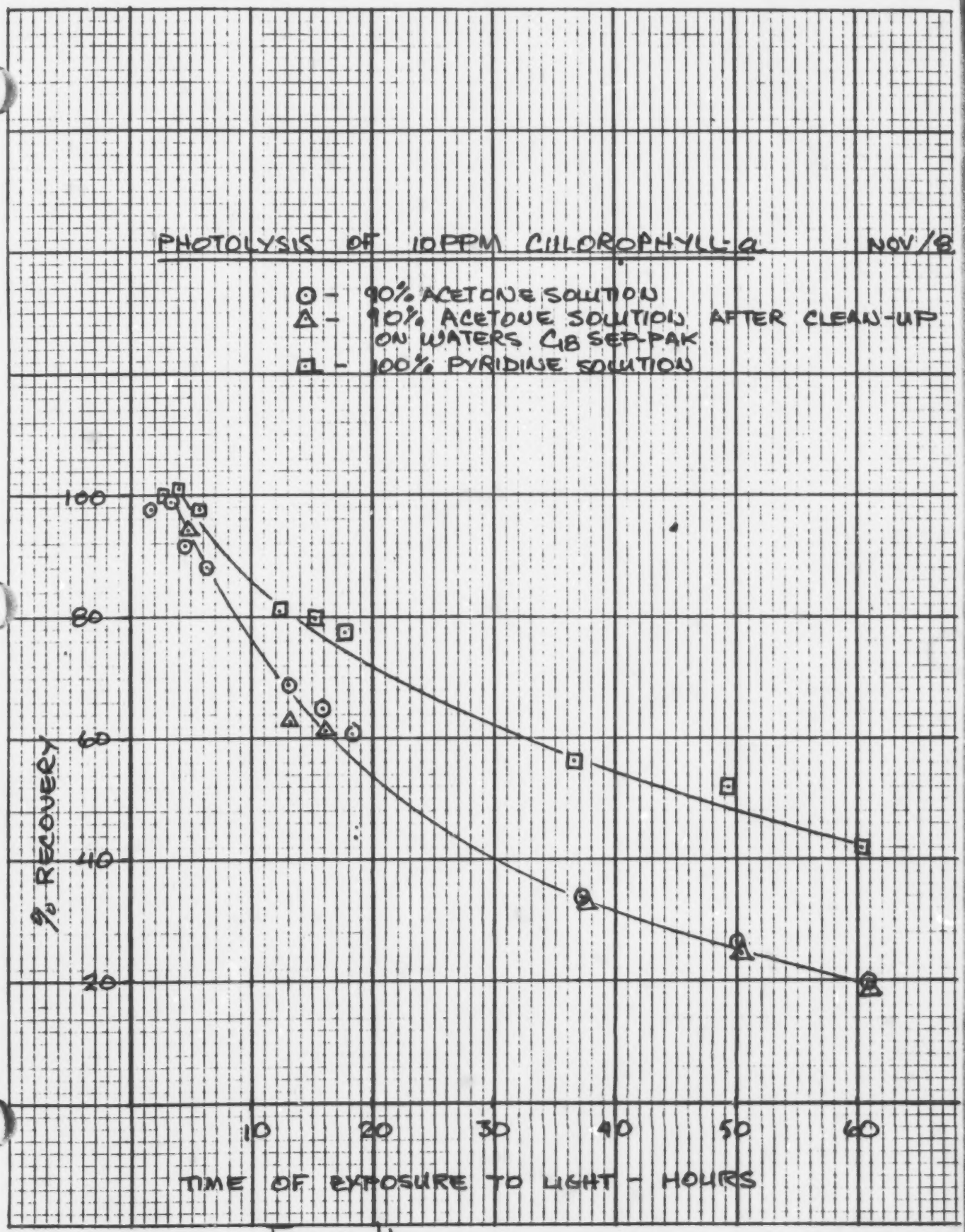

PHOTOLYSIS OF 10PPM CHLOROPHYLL-a
NOV/8
○ - 90% ACETONE SOLUTION
△ - 90% ACETONE SOLUTION AFTER CLEAN-UP ON WATERS C18 SEP-PAK
□ - 100% PYRIDINE SOLUTION
% RECOVERY
100
80
60
40
20
10
20
30
40
50
60
TIME OF EXPOSURE TO LIGHT - HOURS

Figure 4

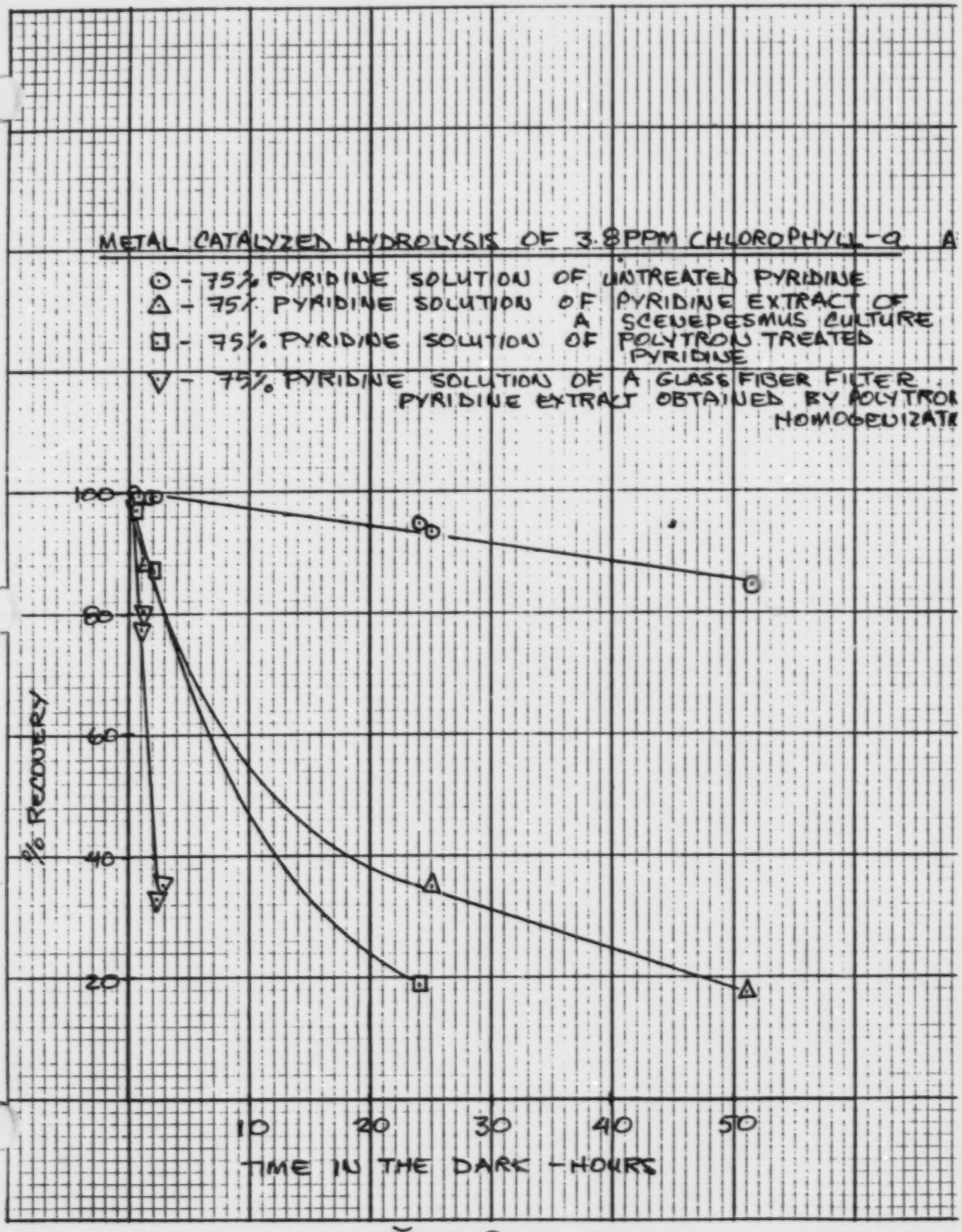

METAL CATALYZED HYDROLYSIS OF 3.8 PPM CHLOROPHYLL-a
⊙ - 75% PYRIDINE SOLUTION OF UNTREATED PYRIDINE
△ - 75% PYRIDINE SOLUTION OF PYRIDINE EXTRACT OF A SCENEDESMUS CULTURE
□ - 75% PYRIDINE SOLUTION OF POLYTRON TREATED PYRIDINE
▽ - 75% PYRIDINE SOLUTION OF A GLASS FIBER FILTER PYRIDINE EXTRACT OBTAINED BY POLYTRON HOMOGENIZATE
100
80
60
40
20
% RECOVERY
10
20
30
40
50
TIME IN THE DARK - HOURS

Figure 3

609: METHOD FOR PHTHALATE ESTERS BY HIGH PRESSURE LIQUID CHROMATOGRAPHY

by

B.K. Afghan, J.F. Ryan and R.J. Wilkinson

INTRODUCTION

The Water Quality Objective Committee of IJC Great Lakes Water Quality has recommended objectives for number of phthalate esters. Linder et al.[1] has reported that acute dibutyl phthalate and diisobutyl phthalate to be in low parts per million levels. Di-2-ethyl benzyl phthalate ester was detected in Atlantic Salmon at levels above 10 ppm. Many agencies in U.S.A. and Canada are collecting some base line data on phthalate esters in aquatic environment.

The analysis of phthalate esters is difficult due to possible contamination from laboratory environment and laboratory materials containing plasticizers. The current methodologies also utilize time consuming cleanup steps prior to quantitative analysis of these compounds.

In our laboratory, we are investigating and evaluating various concentration, cleanup, quantitative analysis and confirmation techniques in order to develop fast, cost effective and accurate method for routine use. This report will summarize the current and future work on this subject. The main emphasis has been on utilization of high pressure liquid chromatography (HPLC) and high resolution gas chromatography (HRGC).

RESEARCH RESULTS

Removal of Lipids and Other Interfering Substances

We have used preparative GPC utilizing styragel column, on extensive basis as an initial step in the cleanup procedure for various organics such as PAH, carbamates, phenols and dioxins. The potential of this approach for phthalate ester was also investigated. The work to date has included optimization of GPC in order to obtain desirable elution characteristics for phthalate esters. Table 1 summarizes the elution order of various compounds including phthalate esters. It should be noted that phthalate esters can be separate from the majority of organic compounds such as OCS, PCBs, phenols, PAH and dioxins. Majority of lipids can also be removed by the preparative GPC.

Alumina and Carbon Fibre Cleanup

The potential of the open column chromatography as well as continuous liquid chromatography using alumina and carbon fibre was also investigated. These systems offer an excellent means of obtaining increased separation of interfering substances and isolating phthalate

esters. These in conjunction with preparative GPC provide a useful cleanup procedure for phthalate esters.

Absorptiometric and Fluorescence Characteristics of Phthalate Esters

Spectrophotometric and fluorescence characteristics were determined using various solution condition. These included solvent effects, pH, oxidation, and reducing conditions. Direct fluorescence was found to be not suitable due to lack of sensitivity. However, it may be possible to enhance fluoresence by derivation. Therefore, UV-absorption was selected as detection system for HPLC.

Analytical Potential of HPLC and HRGC

Number of columns and various chromatographic conditions were used to optimize the separation using HPLC and HRGC. It is possible to develop a fast separation technique using HPLC using ultra-styragel column.

Future Work

Further work will continue on optimization of HPLC in order to achieve the desired separation of phthalate esters, evaluation of derivation technique to improve sensitivity and validation of various cleanup steps using fish, sediment and water samples.

REFERENCES

1. E. Lindén, B-E Bengtsson, O. Svanberg and G. Sundström, Chemosphere, 11/12, 1979, 843.

Elution Order of Various Organic Compounds

Column: Styragel, Particle Size 37-75, Permeability Range 60Å

Mobile Phase - Chloroform Flow Rate = 5 mL/min.

Compound	Fraction Time (min)
Polynuclear Aromatic Hydrocarbons (PAH)	48-56
Phenol	56-65
Pentachlorophenol	45-51
Phthalate Esters	
- DEHP	31-37
- DBP	33-40
- Dnonyl P	30-39
- DEP	36-44
PCBs	43-51.25
Humic and Fulvic Acids	25-32
Lipids and Esters from Fish Concentrate	25-44
1,2,3,4-TCDD	
2,3,7,8-TCDD	
Penta, hexa, hepta and ocata chlorodibenzo-p-dioxins	40-54

610: BURLINGTON WATER TREATMENT PLANTS SAMPLES AND DIOXIN ANALYSES

by

K.A. Terry and F.I. Onuska

INTRODUCTION

Water samples were submitted for organic analysis to determine the taste and odour causing problems in Burlington drinking water.

Research Results

The samples were extracted as soon as possible after using US EPA methodology for Priority Pollutants. This extraction divides the sample into base-neutral and acidic fractions. The samples were analyzed on HRGC-MS in electron impact mode. Resolution was 1200, scan range 60-500 m/z; scan time 2.3 s/dec; with 1.9 kV electron multiplier gain. A 60 m DB-1 WCOT column, 0.32 mm i.d. was used with helium carrier gas. On-column injection was used and the temperature program of 70°C for 9 min. to 280°C at 6°C/minute and hold at 280°C for 20 minutes.

Compounds that were identified matched in retention times and basepeak or pattern of peaks with known standards. For geosmin, the standard obtained did not specify any concentration.

A total of 19 fish and sediment samples were analyzed by HRGC-HRMS for 2,3,7,8-TCDD.

Chromatographic conditions: 30 m x 0.32 mm i.d. DB-1 WCOT column helium carrier gas, temperature programmed 80°C (2 minutes hold) to 220°C at 6°C/minutes. Splitless injection was used. For mass spectrometer hardware multiple ion monitoring was used, resolution was 7000; 2.5 kV electron multiplier, electron impact mode, in current mode operation, scan time 300 msec.

Dioxins were positively confirmed in 10 samples ranging from 2 to 40 ppt.

615: IDENTIFICATION AND DETERMINATION OF TRACE ORGANIC SUBSTANCES IN SEDIMENT CORES FROM THE WESTERN BASIN OF LAKE ONTARIO

F.I. Onuska, A. Mudroch and K.A. Terry

INTRODUCTION

The objective of the present study was to investigate the fate of organic chemicals in sediments of the Western Basin of Lake Ontario, particularly in the fine-grained sediments in the vicinity of the Niagara River mouth, to assess the extent of pollution originating from the Niagara River drainage basin.

The nearshore zone at the Niagara River mouth has been designated by the Great Lakes Water Quality Board a few times in the past as a problem area. A number of industrial discharges to the Buffalo River and the Upper and Lower Niagara River contribute to the pollution of the Niagara River aquatic ecosystem.

Research Results

Sediment cores were obtained at five sampling stations in the Western Basin of Lake Ontario. Cores were subsampled into sections representing surface sediment and a deeper portion of the sediment profile. Extraction of samples was carried out of the base/neutral procedure designated by US EPA.

The base/neutral part of the extract was prescreened by means of HRGC. The identification of individual components was performed by GC/MS technique. A Variant MAT 311A mass spectrometery coupled directly in tandem with a Varian Model 2700 GC was employed for determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin. The major classes of investigated contaminants were chlorobenzenes, aromatics, polycylic aromatics (PAH), alklyated-PAH, alkylated benzenes, phthalates, fatty acid methyl esters, olefins, aldehydes, benzyl esters and benzoates.

The dominant compounds in the alkylbenzene groups were xylenes and trimethylbenzenes, dichloro-; tetrachloro-; and hexachlorobenzenes in the chlorobenzene group, and naphthalene, chrysene, phenanthrene, fluoranthrene and pyrene and their methyl homologs in PNA group.

The relative abundance of individual components in the sediment extracts varied from one station to the other. In the surface sediments, the abundance of contaminants decreased rapidly with the distance from the Niagara River mouth towards the north-west. However, high concentrations of most of the detected organics were present in sediment at the station located east of the Niagara River mouth.

A measurable quantity of 2,3,7,8-TCDD equivalent was present in surface sediment (0-3 m depth) at one station in the vicinity of the Niagara River mouth and in subsurface sediment at a station located east of the River mouth.

Results of the investigation indicate a major transport of organic pollutants towards the east of the Niagara River mouth. However, transport of sediment-associated pollutants exists to a small extent in the north-west direction from the River mouth.

The manuscript was accepted by the Journal of Great Lakes Research and will be published in 9(2) 169-182 (1983).

616: RADIOIMMUNOASSAY TECHNIQUES FOR DIOXINS

by

B.K. Afghan, J.P. Sherry and R.J. Wilkinson

INTRODUCTION

There are several high resolution systems available for the analysis of 2,3,7,8-TCDD and other polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in environmental samples. These systems employ a variety of extraction, cleanup and quantitative confirmatory techniques. The choice of the final analytical technique depends upon the analytical capability and expertise available. Because the quantitative techniques available are time consuming and result in a low sample throughput, they are not suitable for intensive surveys, or routine monitoring of large numbers of samples.

A recently proposed radioimmunoassay procedure (Albro et al., 1979) has several advantages that make it attractive for use in the analysis of dioxins and other organochlorine compounds. Compared to high and medium resolution mass spectrometric methods RIA is simple and inexpensive to perform. Many (up to 30) samples can be analyzed simultaneously. The technique can be made selective by choosing appropriate sera and cleanup procedures.

Not only does RIA have potential in the screening of large numbers of environmental samples for the presence of chlorinated dibenzo-p-dioxins, but with the development of monoclonal antibodies it may prove useful in the confirmation of specific isomers.

Results

A radioimmunoassay laboratory was established at CCIW. The laboratory was equipped with a view towards minimizing man hour requirements and semi-automating some of the assay steps so as to reduce variance between replicates. The gamma counter was modified to accommodate the glass tubes used in the RIA procedure for dioxin.

Procedures were developed for the extraction and cleanup of environmental samples prior to their analysis using RIA and GC/MS.

A set of 40 environmental samples as well as synthetic mixtures containing PCDDs and other contaminants were processed through various concentration and clean up procedures and were then sent to SRI International, Menlow Park, USA for analysis by RIA. The results obtained at SRI were in good agreement with our own data obtained from GC/MS and confirm the earlier findings of Albro et al. (1979) that RIA has potential for the quantitative analysis of PCDDs in environmental samples.

However, a subsequent set of 130 samples that were sent to Dr. Mituma at SRI, in a single blind study, yielded disappointing results: all samples, including TCDD standards, were negative. This sample set was returned to CCIW for eventual inhouse analysis using the RIA procedure.

In collaboration with Dr. Bishai, of the Ministry of Health in Toronto, in house expertise in RIA procedures was acquired. Instrumentation and laboratory procedures were tested and perfected using commercially available RIA kits. Unlabeled 1-N (5-iodovaleramido)-3,7,8-trichlorodibenzo-p-dioxin was acquired from Dr. Apsimon of Carleton University, Ottawa.

The iodovaleramido compound was labeled with iodine-125 at CCIW and antiserum that had been previously obtained from Dr. Albro's lab was standardized against this labeled hapten. The purity of the labeled hapten was examined using TLC. Using the RIA procedure for the detection of chlorinated dibenzo-p-dioxins a standard curve was prepared using unlabeled iodovaleramido dioxin derivative. The resultant curve (Figure 1) suggests that the RIA procedure was functioning correctly in our lab. The smoothing factor (S) and fitting factor (F) were the best possible for an RIA standard curve. The uncertainty in each standard point (weight %) was also acceptably low. A standard curve prepared using TCDD gave a low sensitivity result indicating that a problem may exist with the purity of some of our reagents: either the ^{125}I or Iodovaleramido preparation.

Further work is in progress to solve this problem and to improve the sensitivity and establish the reproducibility of the assay before it is put into operation on a routine basis.

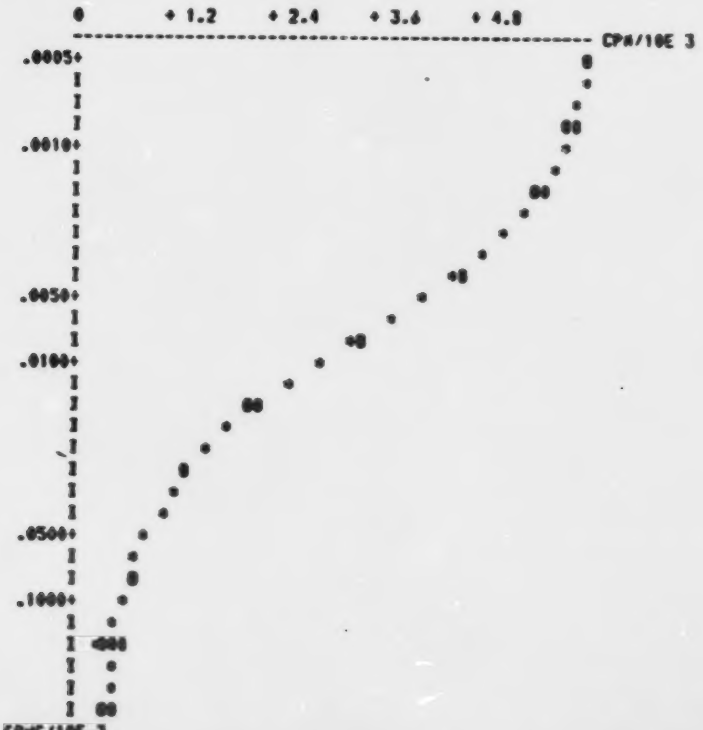
References

Albro, P.W., M.I. Luster et al., 1979. A radioimmunoassay for chlorinated dibenzo-p-dioxins. Toxicology and applied pharmacology, 50, 137-146.

McKinney, J. et al., 1982. Development and reliability of a radioimmunoassay for 2,3,7,8-TCDD. In: Chlorinated dioxins and related compounds, Impact on the Environment. Ed. O. Hutzinger. Pergamon Press, New York, 67-76.

Figure I

```
BLNK      60.0
REFR    6094.0
TOTA   13263.7     B/T= .005   R/T= .459

          CONC       CPM
STD01      .470   5946.000
STD02      .940   5784.667
STD03     1.880   5391.000
STD04     3.750   4536.000
STD05     7.500   3309.333
STD06    15.000   2074.500
STD07    30.000   1309.333
STD08    75.000    705.667
STD09   150.000    497.000
STD10   300.000    398.000


#    S    E  TP
1  .000    1


N =    1
S =    .000
T =   8.008
F =    .000


                                  DIFF.(%)
STAN.    CONC.        CPM          CONC.        WEIGHT(%)

  1       .470       .0000        .0169         .7648
  2       .940       .0000        .0169        1.1172
  3      1.880       .0000        .0042         .8049
  4      3.750       .0000        .0021         .8813
  5      7.500       .0000        .0010        1.0420
  6     15.000       .0000        .0010        2.3861
  7     30.000       .0000        .0014        1.7457
  8     75.000       .0000        .0010        2.5397
  9    150.000       .0000        .0021       10.2813
 10    300.000       .0000       -.0000       11.5578

SUM B =       .0
SUM W =   18935.7
RATIO =      .0000
```



618: REPLACEMENT OF PERCHLORIC ACID IN THE DIGESTION OF FISH FOR As/Se DETERMINATION

by

P.D. Goulden and D.H.J. Anthony

INTRODUCTION

The procedure used for analyzing biological tissue, such as fish, for arsenic and selenium involves a digestion with perchloric acid (1). The safe use of perchloric acid requires special facilities, in particular, the use of a fume exhaust system that can be washed down with water. These have been provided in an isolated location. A recent accident in this area, aggravated by its isolation, not by the use of perchloric acid per se, caused a re-examination of the digestion procedure to see if in fact, perchloric acid was essential in the process. A nitric acid-sulfuric acid digestion, such as that used in the determination of trace metals in fish (2) could be carried out in the general laboratory facilities.

Research Results

In the determination of selenium, if the acid digestion mix is allowed to become in a reducing state the selenium is rapidly lost from the solution. This is indicated by the charring of the residual tissue (3). Examination of the properties of the ternary system, water-nitric-sulfuric acid shows that in most of the digestion procedures used, the amount of water is so large that it is only possible to reach the high temperature necessary for the reaction to proceed by boiling off the nitric acid. At this stage, there is then not enough nitric acid left to maintain the oxidizing conditions essential for selenium retention. It has been shown that by the proper choice of the acid mix the digestion of fish tissue can be carried out with a nitric-sulfuric acid system with complete recovery of the selenium. The same digestion procedure can be used in the determination of mercury and other trace metals.

References

1. Agemian, H. and R. Thomson, Analyst, 1980. 105, 902-907.

2. Agemian, H., D.P. Stutevant and K.D. Austen, Analyst, 1980, 105, 125-133.

3. Gorsuch, T.T., Analyst, 1959, 84, 135.

619: DIOXINS AND BENZOFURANS - METHODS OF ANALYSIS

by

B.K. Afghan, R.J. Wilkinson, J. Sherry and J.F. Ryan

INTRODUCTION

A considerable volume of recent environmental analytical chemistry research on polychlorinated dibenzo-p-dioxins (PCDDs) has been devoted to developing improved methods for the separation and unambiguous identification of various isomers with special reference to 2,3,7,8-TCDD. In addition, increasing attention is also paid to improve the precision and accuracy during quantitative analysis of PCDDs at ultra-trace levels. The analytical scheme for quantitative analysis, for a given matrix, involves several pretreatment and cleanup procedures and those used depend upon the nature of the sample and the relative concentration of interferring substances present in the sample.

In our laboratory, various methods of sample treatment, extraction and cleanup were evaluated in order to develop a suitable analytical scheme which would provide a selective determination of PCDDs by HRGC/ECD or HRGC/LRMS in a wide variety of environmental samples. These include natural waters, sediments, commercial chloro-phenols, wood preservatives, wood shavings sprayed with wood preservative, fish and fine grained sediment and other solid materials such as fly ash.

PCDDs and 2,3,7,8-tetrachlorodibenzo furan (2,3,7,8-TCDF) from above samples are isolated and subsequently separated from interferring substances by various cleanup procedures. The selection of an appropriate analytical technique for a particular sample type depends upon the relative concentration of coextractants.

This report summarizes the evaluation of various concentration and cleanup techniques for wide range of environmental and related samples as well as describing analytical schemes for determination of PCDDs.

Research Results

Extraction techniques: Considerable work has been reported on the recovery and concentration of PCDDs and PCDFs in varoius types of samples. The extraction techniques vary widely from one laboratory to another. In some cases, it is reported similar sample types result in varying recoveries for PCDDs. For example, soxhlet extraction of a sample over long time did not improve extraction efficiency for some samples[1]. Hutzinger et al.[2] studied the extraction efficiency of various solvents for PCDDs and PCDFs and found that it was necessary to pretreat the sample prior to extraction with toluene. A wide vareity of digestion and/or extraction techniques are used by various routine laboratories for extraction of PCDDs and PCDFs from fish tissue and other environmental samples.

In our laboratories, various extraction techniques were evaluated using fish, soil and sediment samples. It was concluded that the selection of the appropriate technique depends upon the nature, size and relative concentration of coextractants in a sample and should be chosen after preliminary testing. For example, it was found that the same extraction technique, used for fine grained sediments (200-325 mesh) gave varying extraction efficiency. The main reason is postulated to be adsorption, chemisorption, coordination/complexation as well as the ability of the solvent to perforate through the sample during the extraction. Figure 1 shows the chromatograms of 10 g sediment samples extracted under different conditions. The samples were soxhlet extracted for 36 hours and the resultant extracts were passed through high pressure GPC using a high capacity styragel column with UV-detection. Those samples treated with trisodium phosphate and sodium sulfate gave the highest extraction efficiency for organic compounds with molecular weight range between ≈ 250-1000.

Lipid removal: Lipids and oxidizable materials are removed by liquid/liquid extraction with sulfuric acid, GPC as well as adsorption column chromatography. The selection of a specific technique depends upon the individual laboratory. These techniques include GPC, sulfuric acid liquid/liquid extraction and Open Column Chromatography utilizing sulfuric acid, sodium hydroxide and silver impregnated silica. μ-styragel and open column chromatographic cleanup procedures do not have high capacity to handle large concentration of lipids and therefore are not suitable particularly when sample size as well as relative concentration of lipid materials is very high in any sample. Preparative high capacity styragel column as well as sulfuric acid liquid/liquid extraction was found to be suitable for samples containing up to 3-4 gram and 10-20 gram of extractable material respectively. The efficiency and elution profile of high capacity GPC was found to be dependent upon viscosity, injection volumne and flow rate. Therefore, continuous monitoring of elution profile of the samples was necessary to determine the type of further cleanup steps as well as collecting an appropriate fraction for isolation of PCDDs from the samples. Similarly, our results confirmed previous findings of Albro et al that concentrated sulfuric acid has a limited capacity for removing lipids and therefore volume of sulfuric acid necessary for removal of the lipid should be based on the actual extractable lipid content. In many cases the amount of sulfuric acid used on impregmentated columns is not sufficient to remove the lipid content from fish extracts.

Removal of phenolic material: The majority of phenolic material is conveniently removed using high capacity GPC. However, in some cases, condensed and high molecular weight phenolic compounds may elute into the same fraction as PCDDs or PCDFs. In addition, some phenoxy-acid, acidic compounds with similar molecular weights as PCDDs or PCDFs and organometallic compounds elute in the same GPC fraction. In this case, trisodium phosphate liquid/liquid extraction was found to be superior to other methods.

Continuous flow chromatography employing sodium hydroxide or cesium hydroxide on silica were also found to be useful. However, these exhibited low capacity for the removal of acidic components. Furthermore, these columns required regeneration prior to reinjecting another sample.

Therefore, these techniques are not suitable, particularly when the relative concentrations of interferences are very high (high µg to mg range).

Alumina Column Chromatography: During the past 4-5 years, we have used micro-alumina column chromatography for the fractionation of PAH from other interfering substances. This involves elution with hexane and subsequent fractionation of PAH by toluene/methylene chloride[4]. Similar columns with modified eluents were found to be suitable for separating majority of PCDDs from interfering substances. In most cases, micro-alumina column was sufficient to remove the majority of organic loading from fish samples with sample sizes as high as 25 g. However, in some cases, a high capacity alumina column was required, particularly when the relative concentrations of the interferences were in high microgram to milligram quantities. The presence of such higher concentration of interfering compounds also affected the elution profile of trace levels of PCDDs (pg-ng range).

HPLC Separations: Conventional HPLC is also used as a suitable technique for cleanup and fractionation of PCDDs and PCDFs. This technique as well as micro-bore HPLC system, was evaluated as a possible means of separating 2,3,7,8-TCDD from interfering substances. Microbore HPLC offered a good potential with particular advantage that significantly smaller volumes and lower flow rates were required to obtain comparable separation.

Carbon Fibre Column Chromatography: Stalling et al.[5] has extensively used this technique for isolation and analysis of PCDDs and PCDFs. This technique offers an excellent final step for the removal of any residual interferences. Carbon fibre chromatography with back elution of PCDDs and PCDFs was found to provide the lowest back ground with HRGC/ECD or GC/MS techniques. In our laboratory this is used as a final cleanup step prior to analysis of PCDDs and/or PCDFs by HRGC/LRMS or GC/ECD screening.

Analytical Schemes for Analysis of Environmental and Related Samples

Sequential columns-multidetection liquid chromatographic system for water and wastewater: This technique is useful where the concentration of extractable material is relatively low (high ng-low µg range). This analytical scheme is suitable for analysis of waters and wastewaters. A suitable aliquot of sample is extracted with toluene and the resultant toluene is dried, concentrated prior to the analysis of PCDDs and PCDFs by this method. The scheme is shown in Figure 2 which utilizes µ-styragel to remove high molecular weight compounds including chlorophyll and majority of phthalate esters. A preselected eluting solvent volume is then passed through cesium and carbon fibre columns. Cesium hydroxide column is used to remove phenolic compounds and the remaining organic compounds are adsorbed on carbon fibre. A sequential elution of carbon fibre with number of solvents removes the majority of interfering substances. The carbon column is finally backflushed with toluene to isolate PCDDs and PCDFs. This fraction is concentrated and made to a small volume in isooctane for analysis by HRGC/ECD or HRGC/LRMS.

Analysis of chlorophenols, wood preservatives and thermal decomposition products of trichlorophenol

The samples are extracted with suitable extraction techniques. The extracted material is finally dissolved in a small volume of chloroform and passed through preparative high capacity GPC. An appropriate fraction is collected to isolate PCDDs and some interfering substances. This fraction is further passed through cleanup procedure consisting of alumina and/or carbon fibre column chromatography prior to analysis by HRGC/ECD or HRGC/LRMS.

Analysis of fish tissues and related materials

A 10-25 g sample size is digested and/or treated with 1N HCl (concentrated HCl also produces comparable results). The resultant mixture is extracted overnight with toluene and centrifuged for 15-20 minutes to separate solid material, aqueous phase and toluene. The solid material is reextracted twice with polytron homogenizer using toluene. The resultant toluene extracts are combined and passed through high capacity GPC, alumina cleanup and carbon fibre chromatography prior to analysis by HRGC/ECD and/or HRGC/LRGC MS.

Analysis of sediment and related materials

Sediment sample is stirred with 150 ml of 1N HCl acid for 10 minutes, centrifuged and washed with deionized water. The treated sediment sample is dried at room temperature and mixed thoroughly with 20 g of anhydrous sodium sulphate. The resultant mixture is extracted with toluene using a soxhlet apparatus. The washings are extracted with 2x50 mL toluene. The toluene extracts are combined and concentrated to nearly dryness. The resultant material is dissolved into small volume of chloroform. In some cases clarification kit may be used to remove particulate matter. The resultant extract is passed through high capacity GPC trisodium phosphate extraction and alumina carbon cleanup prior to analysis. Great care must be exercised to ensure that these columns do not become over loaded by coextractants, resulting in the loss of PCDDs, due to the change in the elution profile as well as loss of the efficiency of the columns. This may also apply in some fish tissues containing high levels of lipids and coextracting interferences.

Current Work

A number of spike fish samples are being processed through the analytical scheme to establish the recovery and precision of this method. Similar recovery and validation studies will be carried out for natural waters, sediments, fly ash and other samples using the above analytical schemes. Figure 3 shows the typical results for the spiked fish sample processed through the procedure as mentioned above.

ACKNOWLEDGEMENTS

The authors thank Mr. A.S.Y. Chau of Quality Assurance and Methods Section for providing sediment samples and staff of Analytical Service Section of Water Quality Branch, Ontario Region, for analysis of some of the extracts.

REFERENCES

1. G.F. Van Ness, J.G. Solch, M.L. Taylor, and T.O. Tiernan, Chemosphere, 10, 1980, 553.

2. R.M.M. Kooke, J.W.A. Lunstenhouwer, K. Olie, and O. Hutzinger, Anal. Chem., 53, 3, 461.

3. P.W. Albro and B.J. Corbett, Chemosphere, 7, 1977, 385.

4. B.K. Afghan and R.J. Wilkinson, "Methods for Determination of Polynuclear Aromatic Hydrocarbons in Enviromental Samples (HPLC-Multidetection System), Manuscript 20-AMD-3-81-BKA, can be obtained from National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario.

5. M.A. Ribick, L.M. Smith, G.R. Dubay and D.L. Stalling, Presentation and subsequently published work in the Proceedings ASTM Sponsored Symposium on Aquatic Toxicity, October 1979, Chicago, Illinois.

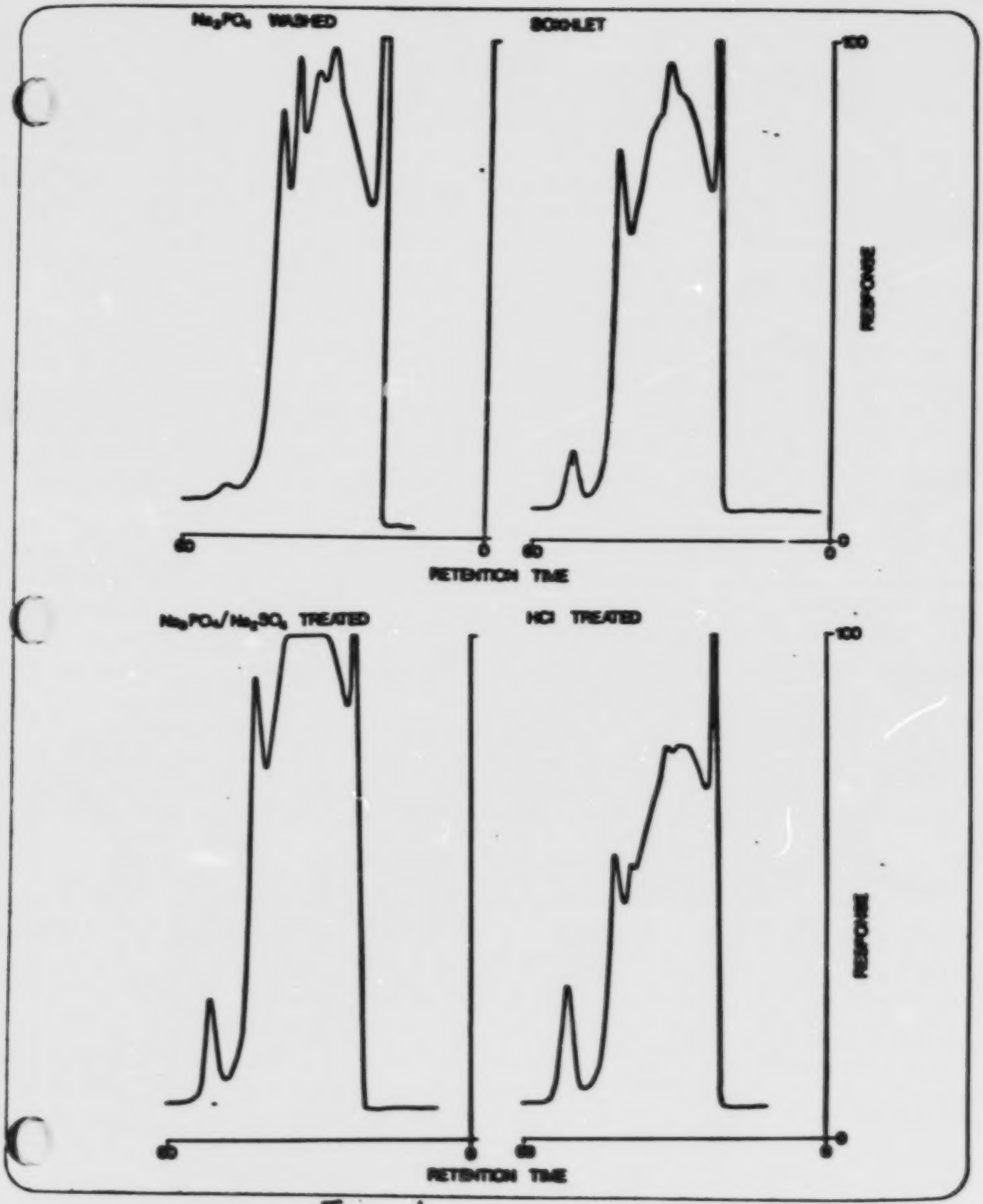
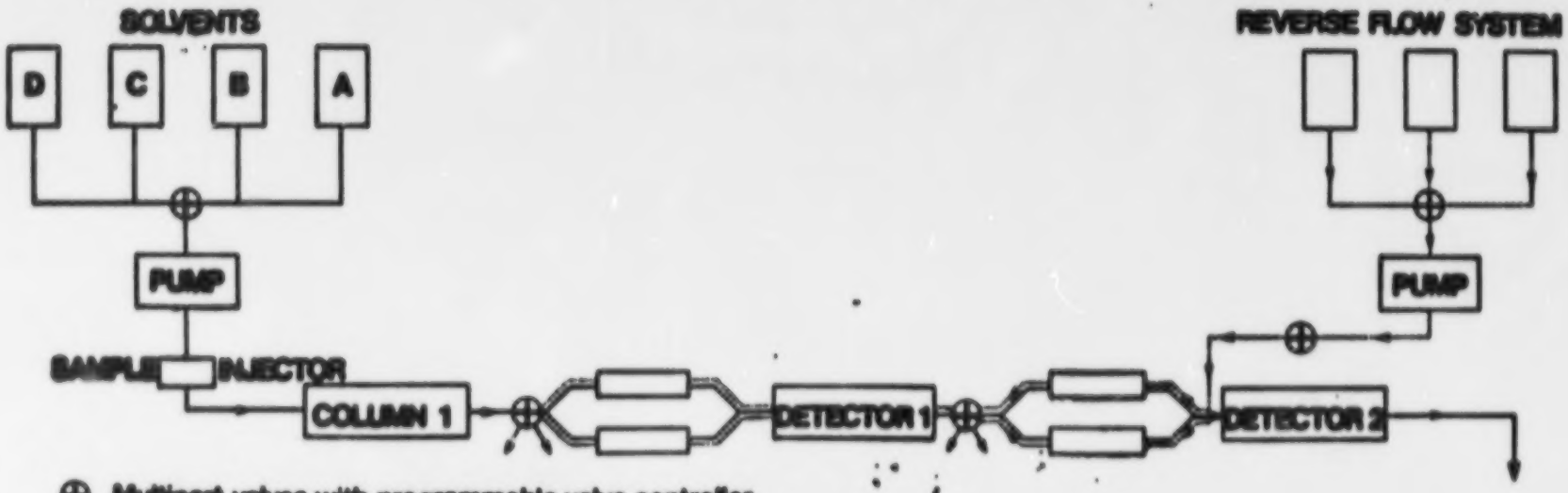

Na_3PO_4 WASHED
SOXHLET
100
RESPONSE
0
RETENTION TIME
Na_3PO_4/Na_2SO_4 TREATED
HCl TREATED
100
RESPONSE
0
RETENTION TIME

Figure 1

MULTISOLVENT–MULTICOLUMN CLEANUP SYSTEM UTILIZING LIQUID CHROMATOGRAPHY



⊕ Multiport valves with programmable valve controller.

– Sample introduction for Eluting System. Number of column(ranging from 1–5) can be employed with the Multi–solvent Gradient System.

– A Reverse Flow Solvent Delivery System for regeneration of columns and back elution of determinands.

Figure 2

Fish Sample → [illegible]

MID RIC + MASS CHROMATOGRAMS
04/27/83 8:38:00 (LABELLED SPIKE)
SAMPLE: 3 UL AF #4
RANGE: C 1.1000 LABEL: N -1. 4.0 QUAN: A 1. 1.0 BASE: U 20. 3
DATA: MY17 01
CALI: MY7 02
SCANS 400 TO 1000

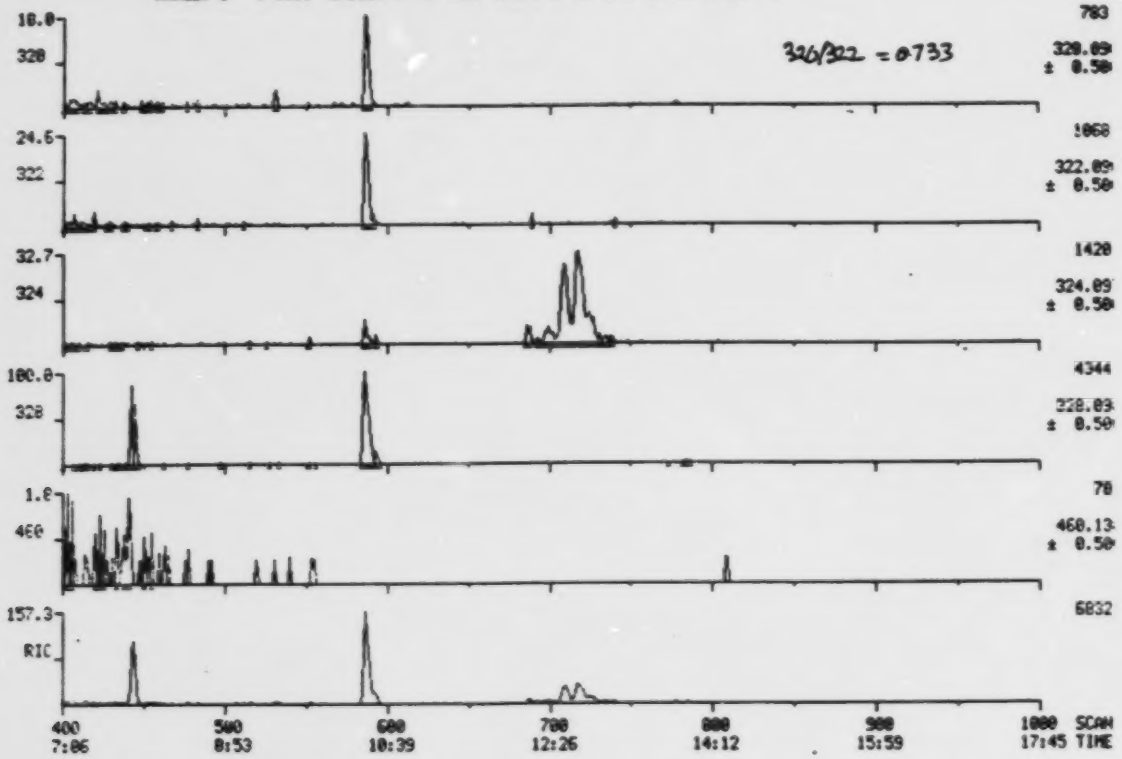
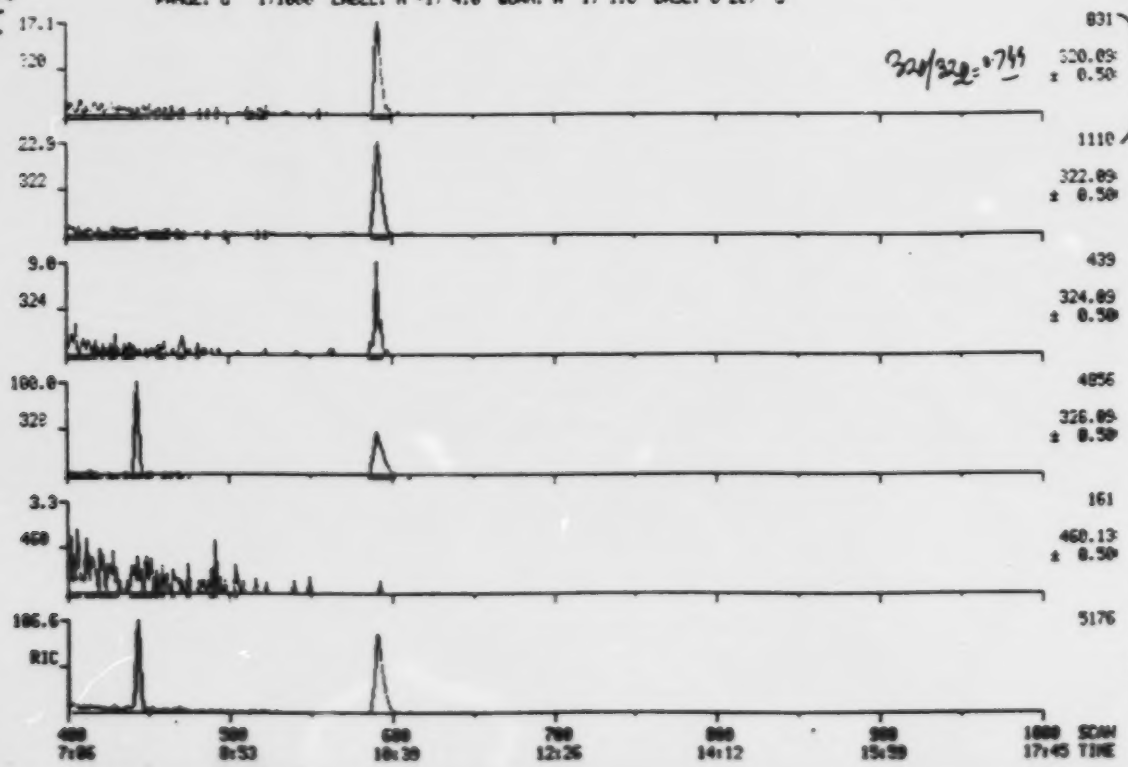


Figure 3

STD → 1:1 Unlabeled and labeled ~25pg/µl

MID RIC + MASS CHROMATOGRAMS
04/27/83 9:39:00
SAMPLE: 3 UL AF #9
RANGE: C 1.1000 LABEL: N -1. 4.0 QUAN: A 1. 1.0 BASE: U 20. 3
DATA: MY19 01
CALI: MY7 02
SCANS 400 TO 1000



Microbiology Laboratories Section

621. MEDIA, WASH-UP, INSTRUMENT AND GENERAL SUPPORT - 1982/82

by

R. McInnis and A. Gadoury

INTRODUCTION

Microbiological procedures are very heavily dependent on a constant stream of consistent media, which often must be prepared on very short notice due to sample arrival. Another important requirement of microbiological laboratories is biologically clean glassware. However, as more and more studies in the microbiological laboratories deal with toxicant screening and microbial growth requirements, there is now an ever increasing need for chemically clean sterile glassware which is a time consuming procedure. The objectives of this unit are to provide, as required, media and wash-up support to the Microbiological Laboratories Section, AMD and other NWRI-CCIW units requiring this service. Secondary duties of this section are to monitor and maintain common user equipment in good repair and to maintain the Laboratories bacterial stock culture collection. Due to the nature of the service provided over the past years, it has been accepted by many of scientists not working in the Microbiology Laboratories Section, to use Microbiological Laboratories glassware, e.g. pipettes, tubes and dilution blanks as common user supplies. This at times has caused some hardship when several scientists have stocked up their supplies for impending studies.

Project Results

Over the year we have provided almost uninterrupted service to NWRI and CCIW staff and rarely missed any deadlines. However, due to the cancellation of the term position in the wash-up room, we were forced to close down the wash-up facilities, and stop all support and services to NWRI and CCIW staff. This led to some disruption of scientists work and their complaints at this loss of service resulted in the contracting out of the was-up room support so that by the end of the fiscal year, everything had returned to normal.

During the year, a total of 32,943 petri dishes of agar were prepared, some using commercial media while the bulk of the petri dishes were made from scratch using various chemical formulations. Some media, especially the Legionella media which required many pH readings were very difficult and time consuming to prepare. Also, during the year 55,645 tubes of sterile median and 1851 bottles of broth (1,234 litres) were prepared.

In the wash-up room the following non microbiological laboratories support was provided:

GLBL	210.5 hr (mostly autoclaving)
AMD	141 hr
ECD	185 hr
AED	195 hr
EPS (Canviro)	41.5 hr

Also, over 12,000 buffered dilution blanks (90 mL) were prepared for Microbiological Laboratories staff as well as other scientists.

622: LEGIONELLA

by

B.J. Dutka and K. Walsh

INTRODUCTION

In reviewing the recent outburst of scientific reports on the Legionella bacillus, it would appear that the natural habitats of the organism are fresh or stagnant waters. Furthermore, there are indications that this organism readily adapts itself to water distribution systems found in buildings and may proceed to colonize these water lines. This project was undertaken to investigate the distribution of Legionella species in Ontario and Quebec environmental waters, cooling towers and potable water samples collected from a variety of public buildings. As part of this project an evaluation of Legionella enumeration techniques was also to be carried out with the most favourable procedure being documented for eventual inclusion in the future revision of the Microbiological Methods Manual.

Research Results

For this study, 221 water samples were collected from Ontario and Quebec lakes and rivers and 120 water samples from 34 commercial, public and private buildings in Ontario. Of the 112 water samples collected from Quebec and Ontario rivers and inshore lake sites, only one yielded Legionella - Blind River. The 109 lake samples yielded Legionella in Georgian Bay, Lake St. Claire and Lake Ontario (Kingston area, Toronto harbour).

Sixty percent of the 34 commercial public and private buildings which had their water systems tested were found to have Legionella organisms in at least one of the waters tested, e.g. drinking water fountain, shower heads, hot water lines, cold water lines, cooling tower lines. In many instances, similar serotype organisms isolated from the same water lines were found to have different antibiotic patterns.

Analysis of the relationship between some of the chemical and physical parameters tested and Legionella presence or absence indicated that (1) the probability of finding Legionella increases with increasing water temperature to 40°C (2) there is a significant association between pH and Legionella (3) the probability of finding Legionella organisms when particulate organic carbon values exceed 0.60 mg/L is double that when POC values are less than 0.60 mg/L and (4) that the probability of finding Legionella in a water samples increases drastically with the increase in the alkalinity level. An in depth presentation of the above data and complementary longevity studies can be found in the joint Dept. of Environment and Dept. of NH&W report "Legionella Environmental Distribution Patterns and Longevity Studies" by B.J. Dutka, K. Walsh, P. Ewan, A. El-Shaarawi, and R. Tobin.

624

by

Alfred Ewan

INTRODUCTION

Fungi play an important role in degradation and recycling of organic matter. Fungi also grow better under acid conditions than most majority of bacteria. Fungi, however, are sensitive to $SO_3^=$ and HSO_3^- ions which may prevent the anticipating advantage of them in the acidified aquatic environment. This study is carried out in conjunction with another ongoing bacteriological study to obtain the baseline data in the acid and nonacid stressed lakes. This study is to review literatures, and to modify procedures and adapt them to assess the role of fungi in the decomposition of organic matter in the acid stressed lakes. In addition, experiments to investigate:

1. the effect of pH on natural population of aquatic fungi;
2. the effect of acidification on substrate colonization on pHs were initiated.

Results

Literature reviews indicated that there was little work done on the effect of acid precipitation on fungi in fresh water. With the increase of acid precipitation there are evidence of decreased bacterial activity and the icnreased fungal activity. From literature there was evidence that the concentration of metal cations increased with acidity and the increased foliar leaching with lower pH. Baseline data indicate that there was apparently some increase in fungal population during the months of October and December. Laboratory routine mycological procedures were adapted to enumerate total fungal populations and organic matter degraders in the acid stressed lakes. Cellulose, pectate, protein, chitin, lipid and starch degrading fungal populations were low (10 per 100 mL). Preliminary laboratory studies of the effect of pH on natural population of aquatic fungi indicated that:

1. the bench type experiment approach is not suitable since pH dropped as much as 4 units in less than a month;
2. the type and amount of sediment used is critical;
3. easy to create toxic effect.

Preliminary laboratory studies of the effect of acidification on substrate colonization on pHs indicated that:

1. the pH changed during colonization;
2. the buffering capacity of a water body can be restored by using Na_2HPO_4 + Citric acid buffer.
3. the amount of Na_2HPO_4 + Citric acid buffer used is critical.

625: MICROBIAL NITROGEN CYCLE METHODOLOGY

by

INTRODUCTION

Microbial transformations are recognized as important in the cycling of nitrogen and other minerals in a water sediment system. One means of measuring the transformation potential is to enumerate the specific bacterial populations responsible for it.

There is evidence that the methods currently in use for enumeration of nitrifying and denitrifying bacteria may severely underestimate these populations. Before the impact of acid stress on these populations could be determined, it was felt that the methodology should be reviewed. The goals of this study were:

1. to review methodology for enumerating nitrogen cycle bacteria in water and sediments and evaluate against techniques now being used to assess impact of acid rain on aquatic microbial populations;
2. to evaluate pH level and buffering capacity below which nitrification and denitrification processes are hindered or cease in acid stressed waters.

Research Results

The literature review undertaken indicated that for both processes, nitrification and denitrification, the currently used "dilution" or most probable number (MPN) method was the most practical for screening of a large number of samples, but that the media employed and the conditions of incubation could be optimized.

Progress was seriously delayed on the nitrification portion of the work due to detainment and nonviability of cultures for preliminary experiments, but experiments are underway to compare media of different formulation, and a revised method should be passed to Dr. Rao for field testing in a Lake Superior cruise in July 1983.

Our currently-used medium for denitrifiers, "Alexander's" medium was compared with two complex media, nitrate broth and "YPN" broth as per recipe by Abd-el-Malek et al. in the processing of over fifty water and sediment samples in the pH range 4.0 to 8.3. In no instance where there was a difference in response, did Alexander's medium show improved recovery over the complex media and in only seven instances did the Alexander's medium match either of the other two in response. The nitrate broth surpassed the YPN broth in response and is recommended for this reason. It is also convenient as it is available in prepared dehydrated form. Agar

plugs layered over the broth provide better maintenance of anaerobic conditions than does liquid paraffin and allows good observation of gas development without the use of Durham tubes. Based on our studies, the use of nitrate broth will be recommended and appropriate modifications will be made in the methods manual.

Studies to evaluate the lower pH limit of nitrification and denitrification processes have been initiated but no results are available at the end of the fiscal year due to the 21 day incubation period required for this test.

628: BACTERIAL WATER QUALITY SURVEILLANCE - LOWER LAKES (LAKE ONTARIO

by

S.S. Rao and A.A. Jurkovic

INTRODUCTION

Great Lakes International Surveillance Plan (GLISP) was developed to satisfy the general objectives outlined in the IJC Water Quality Agreement. The plan or program provides Water Quality information for determining local or whole lake response to control measures. Microbiology Laboratories, CCIW, have provided the IJC information on the nearshore-offshore bacteriological water quality conditions in the International Great Lakes. During 1976, extensive surveys of Lake Ontario were made and a comprehensive report on the bacteriological water quality of the lake was submitted to the IJC surveillance subcommittee. It was proposed to provide a follow-up information in 1982/83. This information will form a basis for setting up non-degradative water quality objectives. During 1982 and 1983, many lake-wide surveys were made to assess the distributions of bacteria of public health significance (fecal coliforms, fecal streptococci and pseudomonas aeruginosa) and eutrohpic indicator organisms (aerobic heterotrophs).

Survey Results

Based on the data, there is no significant difference in densities and distributions of bacteria of public health significance. Some inshore areas (near metropolitan Toronto, Niagara River mouth, Oswego and Black River Bay) can still be considered as potential problem areas. Values for heterotrophs near Black River Bay have been consistently high in numbers over the last 2 years. Based on the bacterial distribution pattern, it is suspected that Lake Ontario may not be experiencing an overall significant increase of limiting nutrients, thus allowing the bacterial populations to maintain these levels over the years. The present data also indicate that offshore waters are relatively free of detectable fecal contamination. In general, the study clearly identifies the point sources where introduction of degraded water is suspected as well as delineate areas influenced by the point source inputs. The extent and degree of input of these nearshore areas on the offshore waters of the lake necessitates the continuation of the point source bacteriological studies parallel to surveillance program.

683: ACID RAIN EFFECTS ON MICROBIAL RESPONSE IN AQUATIC ECOSYSTEM

by

S.S. Rao and A.A. Jurkovic

INTRODUCTION

During the last 2 decades, considerable information has been generated on the effects of acid precipitation on fish, phytoplankton and zooplankton in Ontario lakes. However, a similar information on microbial population and processes in these fresh water ecosystems is scarce. Microbial populations are one of the major biological communities participating in the nutrient cycling and assimilation processes. A study was therefore undertaken to ascertain the nature and extent of acid stress on the indigenous bacterial populations and their activity in some Canadian lakes receiving acid precipitation.

Research Results

Microbial processes are essential in food chain and nutrient cycling to maintain a balanced ecosystem. However, pH is one of the major factors affecting the microbial process, thus buildup of organic matter results. Our 1982/83 studies of lakes receiving acid precipitation indicate that bacterial populations and activity (respiration and organic degradation) in these waters were relatively lower than those in the non-acid stressed environments. For example, pH values below 5.5 appear critical for respiring and aerobic heterotrophic bacteria. Acid stress had no apparent effect on total bacterial populations since lakes with pH 7.8 had total bacteria somewhat similar to lakes with pH 3.8. Bacterial distribution patterns and bacterial respiration in sediments of acid stressed and non-acid stressed lakes revealed interesting differences. The top 5 cm layer of sediments of acid stressed Silver Lake (pH 3.8) contained aerobic heterotrophs in the 10^4/mL range. Their densities between 5 and 40 cm where pH was ≈5.5 were relatively larger (10^5 to 10^6 per mL). However, in the nonacid stressed McFarlane Lake (pH 7.1), bacterial populations decreased from about 10^7/mL in the surficial sediments with pH of about 7.1 to about 10^5/mL in the deeper layers where pH is relatively constant at about 6.5. Associated with this low population the sediment respiration in the acid stressed Silver Lake was 10 to 20% lower than that of the non-acid stressed McFarlane Lake. Also, the organic matter content in the surface sediments of acid stressed Silver Lake was nearly 4 times more than that found in the non-acid stressed McFarlane Lake. This buildup of organic matter has been attributed to the inhibition of microbial decomposition processes. The increased storage of organic matter in the sediment is tied in to recycling of nutrients and hence can affect the behavior of the whole lake.

From the above work, it is surmised that lake acidification will reduce bacterial activity and increase organic matter. These parameters can therefore be used to trace historical changes in response of lakes to acid precipitation.

Quality Assurance and Methods Section

642: FICP QUALITY CONTROL STUDIES

by

A.S.Y. Chau and H.B. Lee

INTRODUCTION

An interlab QC study on the analysis of 19 common organochlorinated insecticides routinely analyzed by organic labs was designed. In this study, each lab analyzed six standard solutions in sealed glass ampules and four fortified sediment samples. Test samples were prepared and their homogeneity and design values were confirmed before they were distributed to 22 FICP labs. As of March 31, results from 7 labs were received. A report of this study is in preparation and it will be sent out to the participants by April 15.

All expected goals were achieved on time and all O&M resources were consumed.

643: INTERREGIONAL QUALITY CONTROL PROGRAM

by

V. Cheam and A.S.Y. Chau

INTRODUCTION

As part of the on-going interregional quality control program, aquatic samples are distributed bimonthly for the analyses of a wide range of parameters routinely determined in Water Quality Branch laboratories. This program is designed to detect anomalies and rapidly correct them when found. Data obtained from this program are comprehensively evaluated, problems are identified and the variance between laboratories is documented.

Those problems reflecting deficiency of analytical methodolgy will be investigated in the section as method development project followed by or preceeded by a special quality control study.

Random and systematic errors are estimated by monitoring the results obtained from paired samples and results are quickly made available to each laboratory to enable them to compare their performance with other Water Quality Branch laboratories. With the development of more reference materials and certified reference materials, considerably more information (e.g. accuracy) can be obtained by appropriate incorporation of these materials into the studies. Nine QC studies for the 5 WQB regional laboratories have been conducted.

Specification of Precision, Accuracy and Detection Limits

The majority of analytical methods used in Water Quality Branch laboratories have precision, accuracy and detection limit statements based on single operator intralaboratory measurements. Such measurements are generally precise while data from different laboratories may show significantly large biases. To further aid the interpretation of data stored in the National Water Quality Data repository (NAQUADAT) statements based on round robin interlaboratory data produced by Water Quality Branch regonal laboratories are needed to establish the reliability of these data.

Since QAMS is a quality control and methods validation group, they were assigned the responsibility of designing and conducting studies to generate specification statements.

The activities for this program have been curtailed so that resource can be spent on the development and conducting of a continuing special quality assurance program for the Prairie Province Water Board laboratories to establish compitability of data generated by these western provincial and federal laboratories. Seven PPWB studies have been sent out (see 654).

Research Results

A manual for the bimonthly quality control studies (for in-house use only) was written to lay out the foundation of the policy and mechanics to efficiently run the Inter-regional Quality Control program.

An additional special interlaboratory quality control study on soft and colored waters pertinent to LRTAP watershed study areas was initiated and finalized along with the regular bimonthly studies. Several problem areas were discovered, the most persistent being SO_4 determination in colored waters which in turn lead to gross differences in ionic balances. The findings have led to a future study forecast to be carried out in order to shed more light into the problem of SO_4 analysis in colored waters.

Problem areas diagnosed by this and other bimonthly studies were reported and brought to the attention of WQB lab managers and headquarters.

A quality control chemist is being trained, whenever he's off from the French course, to take up these duties upon his return to full-time employment.

References

V. Cheam and A.S.Y. Chau, "Manual for the bimonthly interregional quality control studies". Environment Canada, NWRI, Manuscript No. 48-AMD-6-82-VC.

V. Cheam, "Special study on soft and coloured waters pertinent to LRTAP watershed study areas - ionic balance, acidity, alkalinity, major ions and physical parameters". Environment Canada, NWRI Manuscript No. 65-AMD-6-82-VC.

V. Cheam. IRQC studies Nos. 82-83. Extractable trace metal methods by solvent extraction technique.

V. Cheam. IRQC studies Nos. 84-85. Major ions, nutrients and physical parameters in water samples and arsenic and selenium in sediment samples.

V. Cheam. IRQC studies Nos. 86-87. Trace metals (0.2% and 3% HNO_3 preserved), major ions, nutrients and physical parameters and As and Se in sediment. Environment Canada, NWRI Manuscript No. 41 - AMD-6-82-VC.

V. Cheam. IRQC studies Nos. 92-93. Low levels of trace metals, major ions, nutrients, physical parameters, mercury and total P in natural and spiked water samples.

V. Cheam. IRQC studies Nos. 94 to 95. Major ions, nutrients, physical parameters and trace metals in water samples. Environment Canada, NWRI manuscript 63-AMD-6-83-VC.

644. DEVELOPMENT OF STANDARD REFERENCE MATERIALS AND REFERENCE MATERIALS

by

V. Cheam and A.S.Y. Chau

INTRODUCTION

Nearly every phase in environmental protection and pollution control depends on analytical data. However, it is not sufficient merely to generate data. These data must reliable and interpreted with wisdom and understanding.

Quality assurance must be an integral part of analysis and data interpretation because questionable data results in questionable interpretation which generates questionable decisions or conclusions.

Certified Reference Materials (CRMs) are extremely important and useful for analytical quality assurance. Therefore, the research, development and application of CRMs become one of the key components in our overall QA program.

This project deals with the successful development of the world-first Great Lakes sediment CRMs for As, Se and Hg for the overall quality assurance program at NWRI.

Research Results

Successfully developed was the certified Great Lakes sediment reference material for 3 toxic elements - As, Se and Hg. To our knowledge, this is the first CRM in the world which is certified for all 3 elements altogether for such a substrate.

The certification of a second Great Lakes sediment CRM is nearly finished for As, Se and Hg.

Two water CRMs were developed for common major ions. The stability of the two standards was monitored over a 3 year period.

References

A.S.Y. Chau. Water Quality Bulletin, 8 (1), 26-29 and 53-54 (1983).

V. Cheam and A.S.Y. Chau, "Research development and application of the 1st Great Lakes Sediment RMs for As, Se and Hg". Presented at the 185th ACS National Meeting, Seattle, Washington, March 20-25, 1983.

Extended Abstract, ACS Division of Environmental Chemistry, Vol. 23 (#1), 205-207 (1983).

V. Cheam and A.S.Y. Chau. Analytical Reference Materials. IV. Development and Certification of the 1st certified Great Lakes sediment reference material for As, Se and Hg. Submitted for publication in a scientific journal.

V. Cheam and A.S.Y. Chau. Preparation, homogeneity and stability of major ions in spiked and synthetic standards used for quality control studies. Manuscript to be submitted for approval.

645: METHOD ADAPTATION FOR WQB LABORATORIES (INORGANICS)

by

V. Cheam

INTRODUCTION

Method Development is one of 5 key components of the overall quality assurance program at NWRI. To constantly meet the needs for more reliable measurements of water quality parameters, it develops new methods or adapts or modifies existing ones to fulfill the requirements from Water Quality Branch laboratories.

This project deals with the validation of analytical methods for arsenic and selenium in seaweed.

Research Results

The acids, oxidants and digestion conditions were found efficient to extract As and Se from seaweed and from several certified reference materials.

The project is slowed down considerably to enable time to carry on with the former duty on project 643 and an additional new project of 654 which have higher priority. Project 654 (to design and to conduct QC studies for the Prairie Province Water Board laboratories) is a new project which had to be initiated around September 1982. The new chemist for project 643 is on French training, thus the author has to absorb the duty of this new chemist and, in addition, to provide the proper training.

646: ORGANIC METHOD DEVELOPMENT

by

Y. Stokker, H.B. Lee and A.S.Y. Chau

INTRODUCTION

This study is part of the ongoing work concerning the development of new and/or modified methods for the analysis and quantification of organic and biochemical parameters in a variety of substrates. These methods are directed toward inclusion in the Analytical Methods Manual and for publication in research journals.

Achievement

The position of an organic method development chemist was vacant between 1 April to 31 October 1983. However, work previously done in FY 81/82 and currently done in FY 82/83 by H.B. Lee and A.S.Y. Chau resulted in the preparation of 4 papers (all submitted to and accepted by the JAOAC) and the presentation of 2 papers in the 96th Annual AOAC Meeting (see reference section).

As of November 1, the vacant position was filled by a chemist. The incumbent is a new employee and new to this field of research and has therefore been under in-house training to develop practical knowledge and experience in trace organic analysis. The initial part of this training period consisted of a major clean-up and reorganization of the Organic Methods Development Lab. At the same time, familiarization with equipment, instrumentation and analytical techniques was accomplished by participating in the execution of quality control studies and in the development of sediment reference materials. More specifically, the incumbent at this time assisted in the preparation of thirty (30) sediment extracts for chlorobenzene (CB) analysis by GC-MS and thirty (30) sediment extracts for the quantitative analysis of six (6) World Health Organization (WHO) polynuclear aromatic hydrocarbons (PAHs) by GC-MS. Another twelve (12) sediment samples were extracted and analysed for CBs in order to provide further support data on the CB levels for the certification of these sediment reference materials. This work was extended to include the preparation of thirty-six (36) sediment extracts for the qualitative and quantitative analyses of polychlorinated biphenyls (PCBs) and twenty (20) organochlorinated pesticides (OCs) in these reference materials, and served to provide some experience in capillary GC-ECD techniques.

Currently in progress, is the preparation and training for development of a multi-residue method of analysis for the generation of a multi-class and multi-residue method for the analysis of acid and neutral herbicide in water and in sediment in 1983/84.

References

1. Analysis of Trifluralin, Diallate, Triallate, Atrazine, Barban, Diclofop-methyl, and Benzoylprop ethyl in Natural Waters at Parts Per Trillion Levels by H.B. Lee and A.S.Y. Chau. J.A.O.A.C., 1983. In Press.

2. Analysis of Pesticide Residues by Chemical Derivatization. VI. Analysis of 10 Acid Herbicides in Sediment by H.B. Lee and A.S.Y. Chau. J.A.O.A.C. 1983. In press.

3. Analysis of Pesticide Residues by Chemical Derivatization. VII. Chromatographic Properties of Pentafluorobenzyl Ether Derivatives of 32 Phenols by H.B. Lee and A.S.Y. Chau. J.A.O.A.C. 1983. In press.

4. Analysis of Trifluoralin, Diallate, Triallate, Atrazine, Barban, Diclofop-methyl, and Benzoylprop ethyl in Sediments at Parts per Billion levels by H.B. Lee and A.S.Y. Chau. J.A.O.A.C. 1983. In press.

5. Multi-residue analysis of 10 acid herbicides in sediment by H.B. Lee and A.S.Y. Chau, presented at the 96th Annual AOAC Meeting, Washington, D.C. 1982.

6. Analysis of Seven Neutral Herbicides in Water at Parts Per Trillion Levels by H.B. Lee and A.S.Y. Chau, presented at the 96th Annual AOAC Meeting, Washington, D.C. 1982.

653: IJC QUALITY ASSURANCE

by

K.I. Aspila

INTRODUCTION

Over 50 laboratories within the international Great Lakes Basin contribute data in support of the Canada-U.S. Great Lakes Water Quality Agreement. These data from different laboratories are quite often merged for whole lake definition of quality. Some data, accumulated over years, are being used to define trends in environmental pollutants. The definition of trends and the successful merging of data sets are possible only if laboratories are comparable (free of bias) and the lab measurements are in control. Effective interlab comparison studies delivered on a timely basis define both control and overall lab performance. This information is essential for the several hundreds of laboratory analysts, the several dozen primary users of data and the various program managers responsible for the Great Lakes environmental projects. If laboratory data are biased, or erratic or if the laboratory is out of control, the data is worthless. In fact, bad data are worse than no data at all since data will "taint" the data banks and yield false decisions in the future.

This project supports the efforts of the IJC Data Quality Work Group of the Water Quality Programs Committee. Three interlab studies (major ions, trace metals and total phosphorus in water) were scheduled for FY 82/83. This project also included the acquisition, through contract analysis, of analytical data on a Great Lakes reference sediment destined for certification.

A simple interlab study involving one or two samples and a couple of labs very often yield misleading information since comparable data may still be dead wrong (severe bias). Furthermore the existence of in-lab QC protocol does not alone assure technically valid data. This IJC project on the other hand addresses a multisample approach (10 to 15 reference samples) many labs (20 to 35) and includes many constituents (10 to 20). By use of stable references and inclusion of certified reference materials (if available) the peer group assessment of performance is very rigorous and definitive on bias and comparability. The interpretative technique used is very automated and utilizes nonparametric statistics developed by Dr. Youden and widely used by the AOAC and NBS (1). This interpretative process (2) has been expanded to include the flagging of results that deviate significantly from a median concentration.

Accomplishments

A. Five interlab studies were prepared and distributed rather than the three scheduled. The five studies were as follows:

Study # 35 - Toxic Organics in Fish
- initiated new study w/samples - Oct. 12, 1982 (19 labs)
- letter of evaluation (in progress) (labs responded)

Study # 40 - Total Phosphorus in Water
- Initiated new study w/samples - June 18, 1982 (34 labs)
- Letter of evaluation - Oct. 14, 1982 (24 labs responded)

Study # 41 - Selected Major Ions, Nutrients, and Physical Measurements in Water
- Initiated new study w/samples - July 6, 1982 (33 labs)
- Letter of evaluation - Oct. 18, 1982 (23 labs responded)

Study # 42 - Total Metals in Water
- Initiated new study w/samples - Aug. 30, 1982 (27 labs)
- Letter of evaluation - Feb. 21, 1983 (16 labs responded)

Study # 43 - Total Phosphorus in Water
- Initiated new study w/samples - Aug. 30, 1982 (36 labs)
- Letter of evaluation - Jan. 7, 1983 (24 labs responded)

Study # 44 - Total Phosphorus in STP Effluents (scheduled for FY 83/84)
- In preparation - approximately 40 labs participating

Each of the above completed studies have produced letters of evaluation specific to each participant on each constituent analyzed. In the case of contract labs, letters have been addressed to the scientific authority. Users of data who wish to seek information to assist in verifying laboratory capabilities (bias and control) need only to solicit feed back from the lab providing them their Great Lakes program data. Files on each study are also maintained in the IJC Great Lakes Regional office in Windsor.

B. Information, through contract analysis, on the constituent concentrations of PCB, chlorobenzenes, and polyaromatic hydrocarbons have been obtained for the Great Lakes reference acquired and processed in the previous year. This new information will be valuable for preparing an effective interlab study on toxic organics in sediments in FY 83/84 (if resources are available).

References

1. W.J. Youden, "Ranking Laboratories by Round Robin Test" in Precision Measurement and Calibration, NBS Special Publication 300, Vol. 1, Editor H.H. Ku, U.S. Dept. of Commerce, Issued February 1969.

2. "Evaluation of Performance of Laboratories Determining Water Quality Constituents through Natural Water Samples whose True Values are Unknown". J.L. Clark; in Environmetrics 81. Alexandria, Virginia, April 8-10, 1981.

654: PRAIRIE PROVINCES WATER BOARD QUALITY ASSURANCE PROGRAM

by

V. Cheam and A.S.Y. Chau

INTRODUCTION

Under the auspices of the Prairie Provinces Water Board, a program is initiated for assessing and improving the comparability of water quality data generated by the Federal WQB Calgary Lab (ECS) and the Alberta, Saskatchewan and Manitoba provincial laboratories.

In the first phase of this program, interlab studies are designed and conducted bi-monthly on some 40 parameters involving some 100 analytical procedures.

Research Results

The first study was successfully planned, initiated and carried out as schedule. Subsequent studies are also on schedule.

A computer program, STAT2, was developed in order to handle the extra interlaboratory data from Prairie Provinces laboratories. It's efficient for use to compile, compute and report interlab data.

Additional resources when available next fiscal year will be used to develop another computer program to integrate data from various studies to generate statistical evaluation on laboratory performance and assessing method compatability. Additional resource will also be used to develop and prepare various reference materials and certified reference materials so that accuracy of data can be calculated. It may be pointed out that each quality control study, due to the necessarily simple design for fast feed back, cannot by itself provide information on precision, accuracy and data compatability. It only provides a quick warning system to each laboratory of analytical problems and to show data comparability. With an integrated design, and suitable computer programming, information on precision and data compatability will be available when enough data from several studies are integrated. If sufficient resource is available, more RMs and CRMs can be developed to define accuracy of data as well.

References

1. Prairie Provinces Water Board Water Quality Analytical Methods Task Force. Task Two Report. April 1981.

2. V. Cheam. "PPQC Studies Nos. 1 to 2 - Trace metals analysis by both direct aspiration and solvent extraction techniques, and analysis of major ions, nutrients and physical parameters in spiked water samples". March 1983.

3. V. Cheam. Several preliminary reports were distributed to lab managers to highlight and update the status of each study. Problem analyses were singled out.

657: INTERLABORATORY QUALITY ASSURANCE PROGRAM

by

H.B. Lee and A.S.Y. Chau

INTRODUCTION

This continuing project concerns with various aspects of inter-laboratory QC programs related to the analysis of toxic organics. The two major activities in this project are: (1) designing and implementing interlab QC studies for the analysis of toxic organics, and (2) research and development of certified reference materials for major organic environmental pollutants.

Achievement

(1) Interlab QC Studies

A national QC study on the quantitation of total PCBs in sediment extracts and standard solutions was conducted. A total of 27 labs provided results on eight test samples. A summary report was sent to all participants providing results. The results of this study again indicated that quantitation of PCBs remained to be a major source of analytical error in such analyses.

Another national QC study on the analysis of common OC pesticides was designed. A total of 6 standard solutions and 4 fortified sediment samples were distributed. As of March 31, nine labs had already supplied results. A final report will be prepared when the study is closed.

(2) Development of Sediment Certified Reference Materials (CRMs) for Organics

(a) Chlorobenzenes

In this continuing effort to develop and certify a reference material for chlorobenzenes, about 50 in-house repetitive analyses of the first CRM were performed by Soxhlet extraction and capillary column GLC analysis. The data collected indicated the presence of ng/g levels of dichloro-, trichloro-, tetrachloro-, pentachloro- and hexachloro-benzenes together with hexachlorobutadiene in this natural sample. Thirty sediment extracts of these materials were also prepared for a contract analysis by GC-MS. The latter was required in the future certification of the CRM as a second independent analytical technique. The contract results received in general agreed with the in-house data.

(b) PAHs

Further contracts (1st phase) on the analyses (HPLC) of the 6 WHO PAHs in our CRMs were generated. Results on 85 samples were received and evaluated. In-house HPLC analyses of these PAHs will be set up so that further work on these sediment CRMs could be carried out. Contract analysis by GC/MS next fiscal year will be needed to complete the second phase of the certification process.

(c) Application of CRMs

Requests of our sediment CRMs have been received from various parties of ACRS of AMD for the research of new analytical methodology. Requests also came from Regional Water Quality Branch Analytical Services Labs (Burlington and Moncton) as well as many other private andprovincial labs for their in-house QC applications. The CRMs were also requested by the Monitoring and Survey Section (WQB) and by GLBL (DFO) for the monitoring of analytical performance of contract labs.

Summary

All expected goals were achieved on-schedule. Financial resources (A-base O&M and capital) were all spent.

Expected Achievement for the Next FY

Please refer to the project forecast for Study No. AMD-657 (FY 83-84).

References

1. Summary Report on Interlaboratory QC Study No. 31 - Analysis of total PCBs in sediment extracts and standard solutions by H.B. Lee and A.S.Y. Chau.

2. "Certified Reference Materials (CRMs) for Environmental Substrates - Research. Development and Application" by A.S.Y. Chau. Presented in the 96th Annual AOAC Meeting. Washington, D.C. 1982.

3. "Development of Sediment CRMs for Toxic Organics of Environmental Importance" by A.S.Y. Chau and H.B. Lee, presented in the 96th Annual AOAC Meeting, Washington, D.C. 1982.

659: LRTAP QUALITY ASSURANCE

by

K.I. Aspila and S. Todd

INTRODUCTION

The Federal-Provincial Long Range Transport of Atmospheric Pollutants Program is a large integrated effort involving many different laboratories who contribute data to define the impact of and the trends in environmental pollutants. If this information is to be useful it is imperative that the data base be comparable between labs and between years. This project responds to this need by providing reference samples for analysis and interpretation. When results are reviewed it is possible to define comparability and performance (1,2) of the contributing laboratories. When the review process is rapid, it allows for corrective action to be taken by lab managers to reduce or remove bias and improve performance. If bad data is left unchecked it will taint present and future data bases. Bad data are useless and retards the decision process on trends and impacts.

Study L-1: Major Ions, Nutrients and Physical Parameters

The study consisted of 16 waters obtained from the LRTAP watershed study programs including precipitation, waters from the Great Lakes Basin and two synthetic standards. Analysis was requested for 16 water quality parameters.

Study L-2: Trace Metals in Water

This study consisted of 10 aqueous test samples prepared in 0.2% HNO_3 with analysis requested for twelve trace metals. The design included natural rain, surface waters and synthetic samples.

References

1. W.J. Youden, "Ranking laboratories by round robin test" in Precision Measurement and Calibration, NBS Special Public. Vol. 1, Editor H.H. Ku, U.S. Dept. of Commerce, Issued Feburary 1969.

2. "Evaluation of performance of laboratories determining water quality constituents through natural water samles whose true values are unknown". J.L. Clark, in Envirometrics 81. Alexandria, Virginia, April 8-10.

Computer Services Section

670: COMPUTER SERVICES FOR WATER MANAGEMENT RESEARCH

by

H.C. Pulley, M. Kinder, U. Hamilton, B. Maleed, P. Moody, and J. Foley

INTRODUCTION

Accomplishments

a) System down-time amounted to 18.3 hours. Internal problems (power, water, etc.) accounted for all but 0.8 hours of this down-time. The Cyber was in use for 5003 hours, so the system up-time was 99.6% for the past year.

b) The section's participation in Open House '82 was very successful. During the four days of Open House, over 8000 souvenir calendars were given to visitors. No problems occurred in spite of the heavy traffic through the computer room.

c) Graphics software was developed for the MVI-7 colour terminal which the Data Management Section acquired. This software included Calcomp-compatible subroutines and a version of the General Purpose Contouring Package (GPCP).

d) The plotter version of GPCP was modified to provide a multiple pen capability, so that hard-copy contour plots can be produced in three colours.

e) H.C. Pulley attended the course "NOS Analysis, Version 1-2 Differences" given by Control Data. This provided background knowledge which will be essential in providing a smooth transition from NOS Version 1 to Version 2 in the fall of 1983.

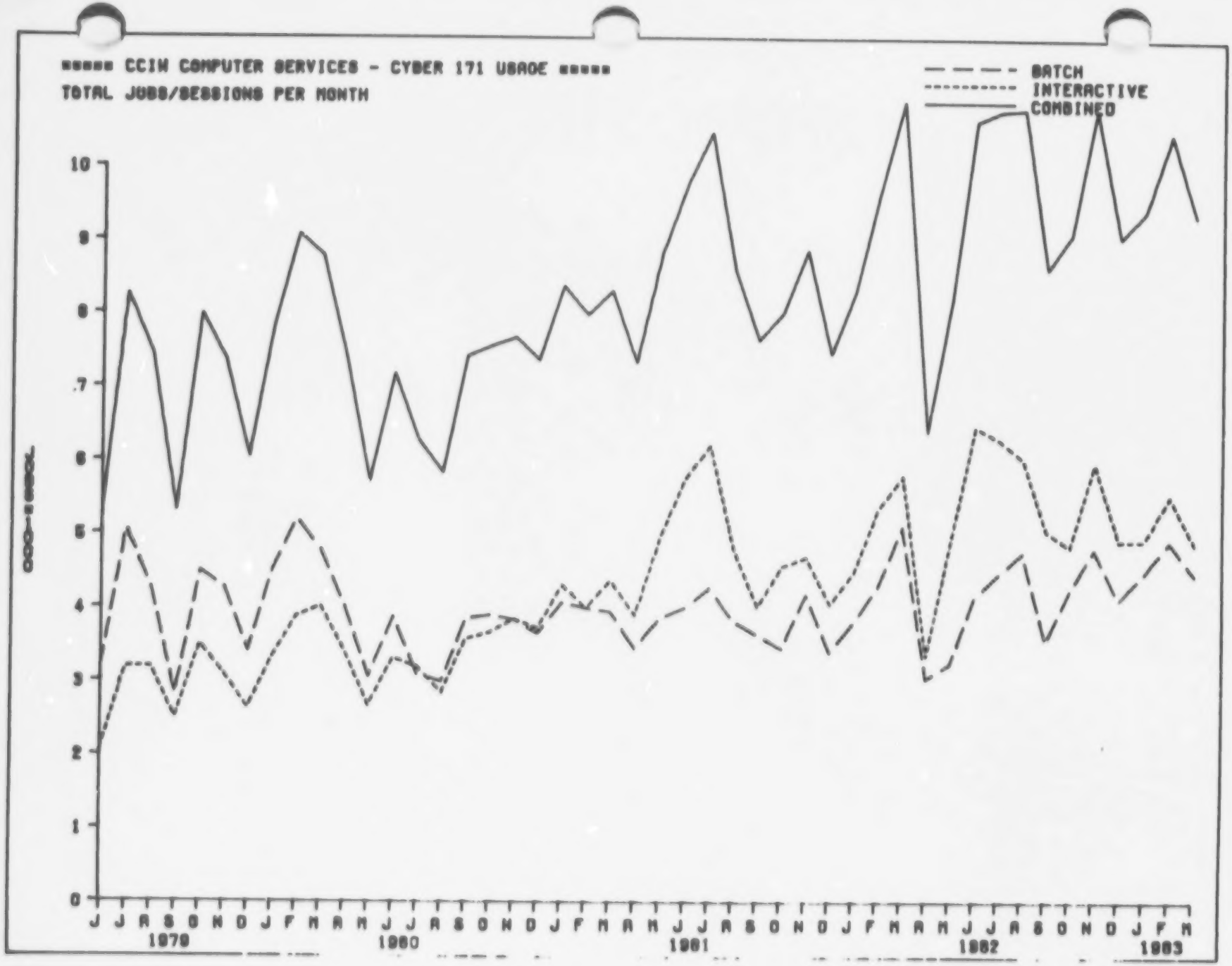
f) In support of the study of future computing requirements at CCIW, detailed analyses were made of System 2000 usage and interactive workload characteristics. A large benchmark program was set up and run here to provide workload and cost comparisons between the Cyber 171 at CCIW and external service bureaus.

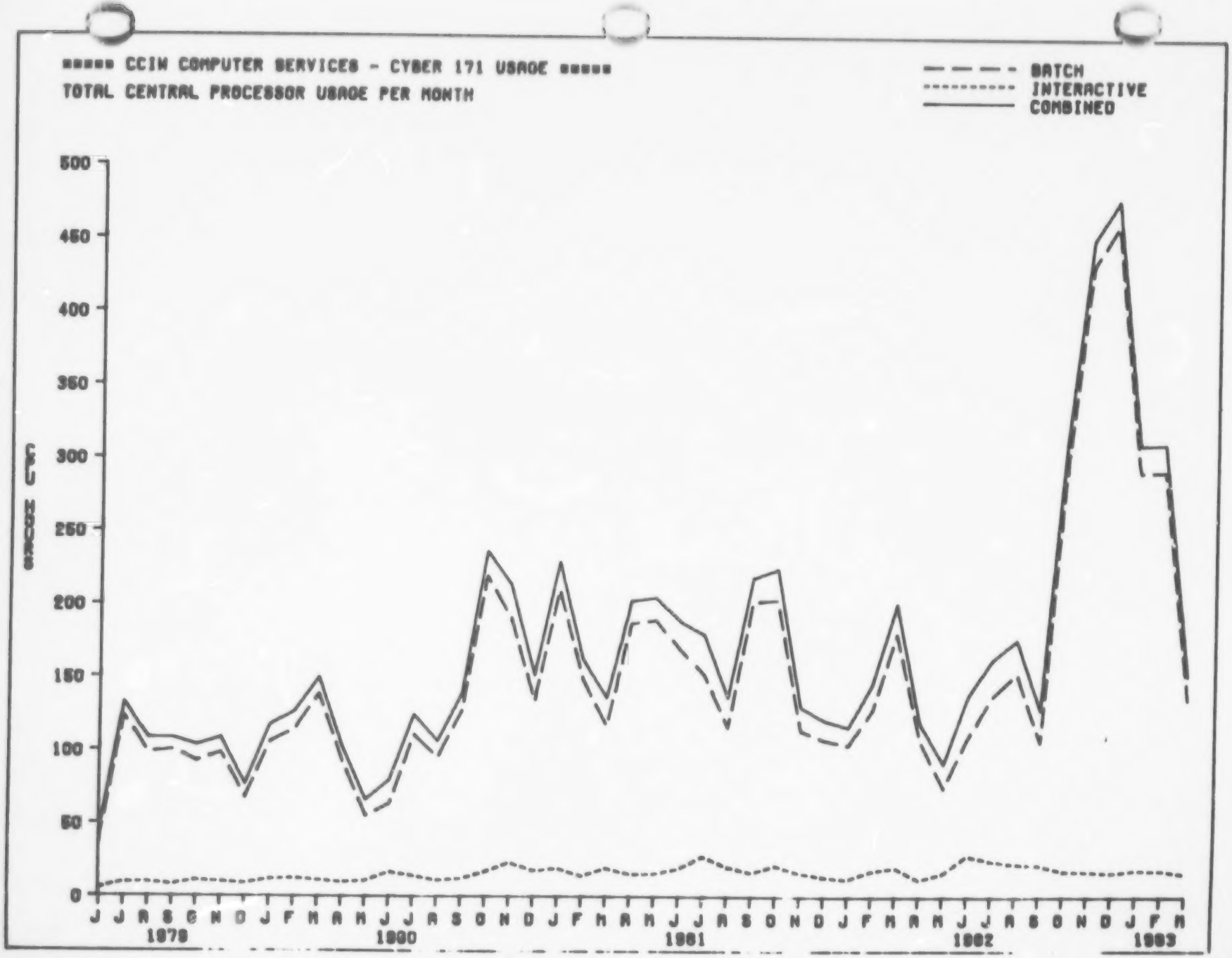
Support Provided

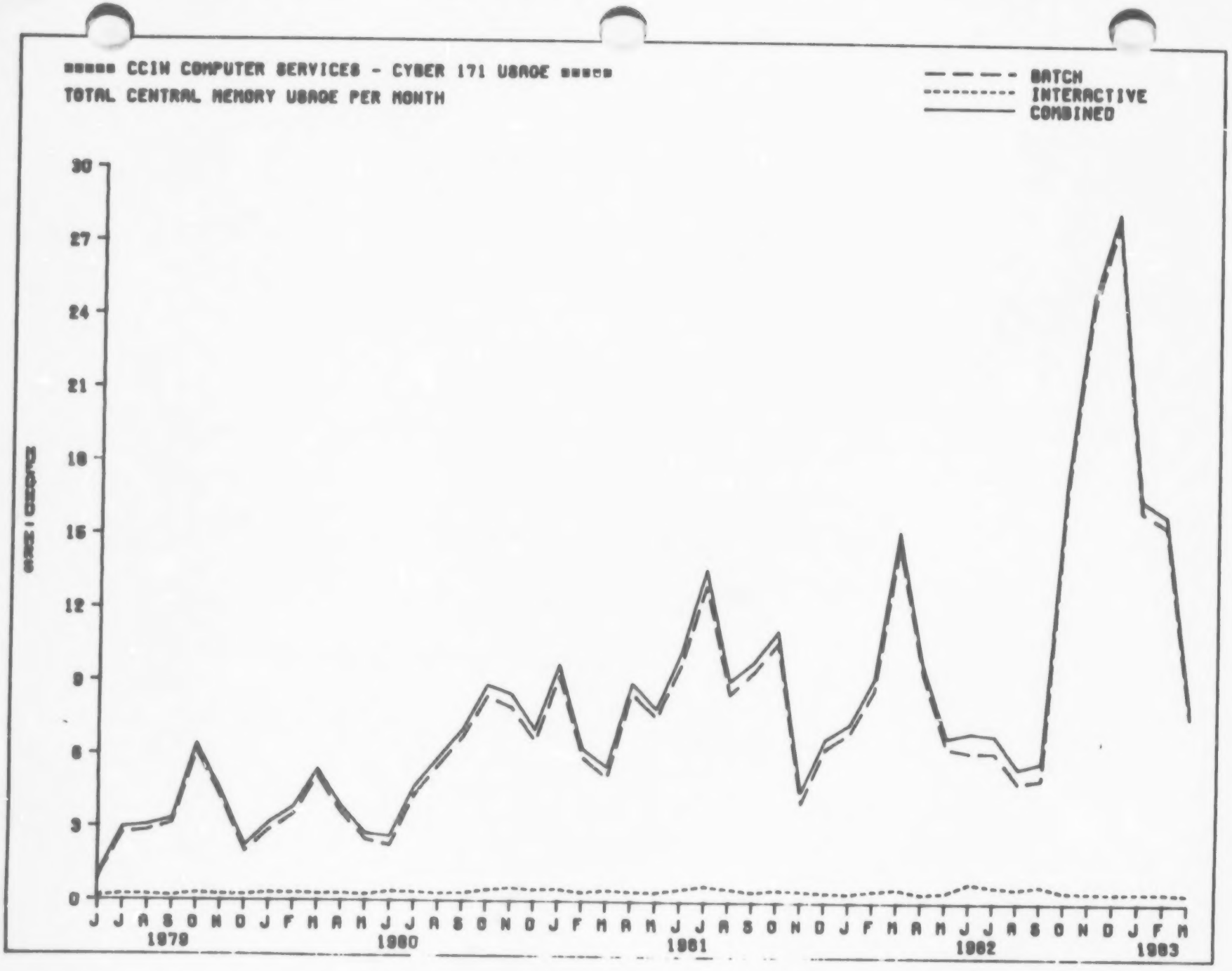
The attached report provides detailed information concerning Cyber 171 usage during 1982/83. Other reports describing total Computer Services usage has already been sent to the division office. The total value of usage was $1,095,665. This represents an increase of 17.5% over 1981/82. Cyber 171 usage in 1982/83 increased by 32.8% over 1981/82.

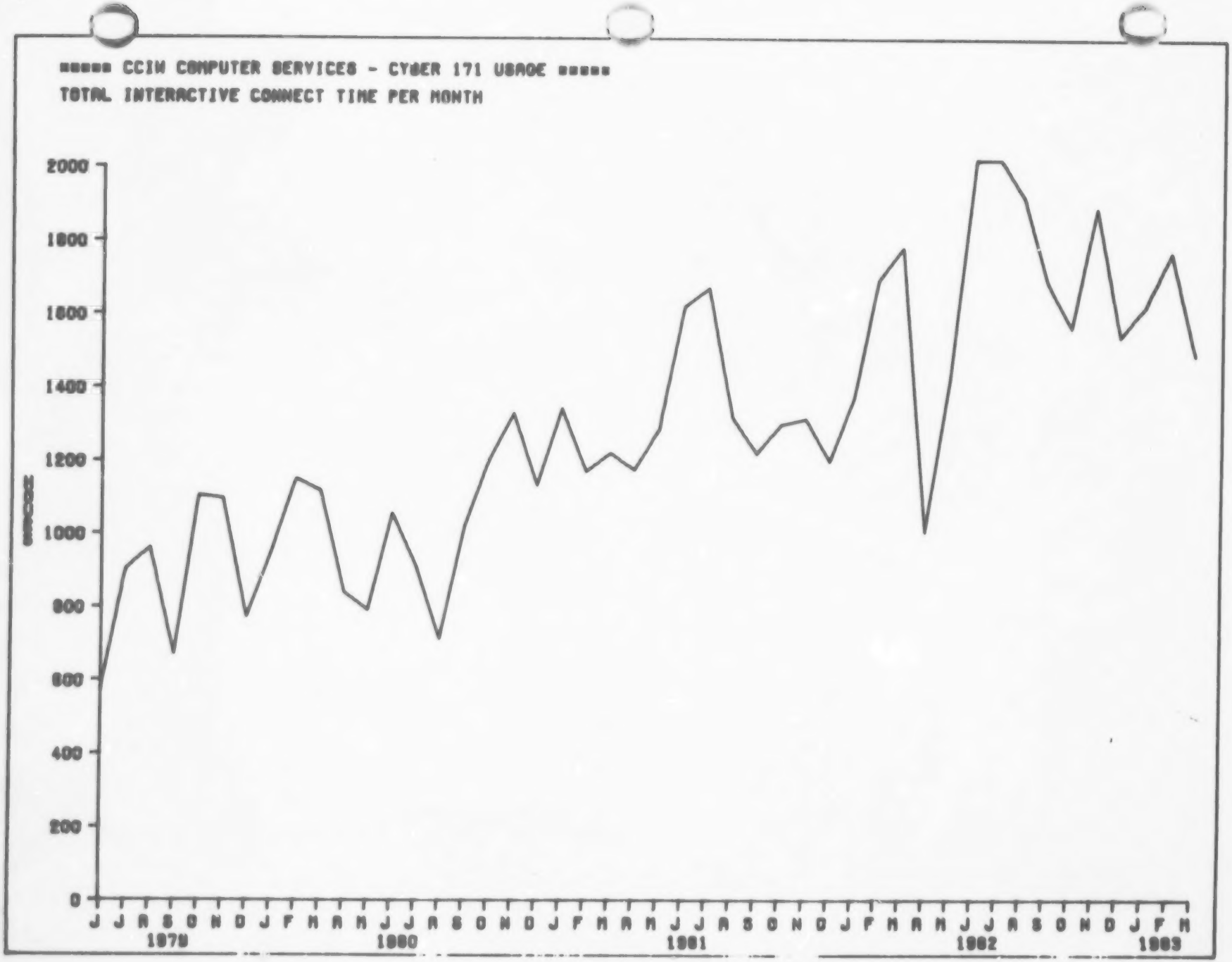
Usage by non-NWRI components of CCIW increased slightly during 1982/83.

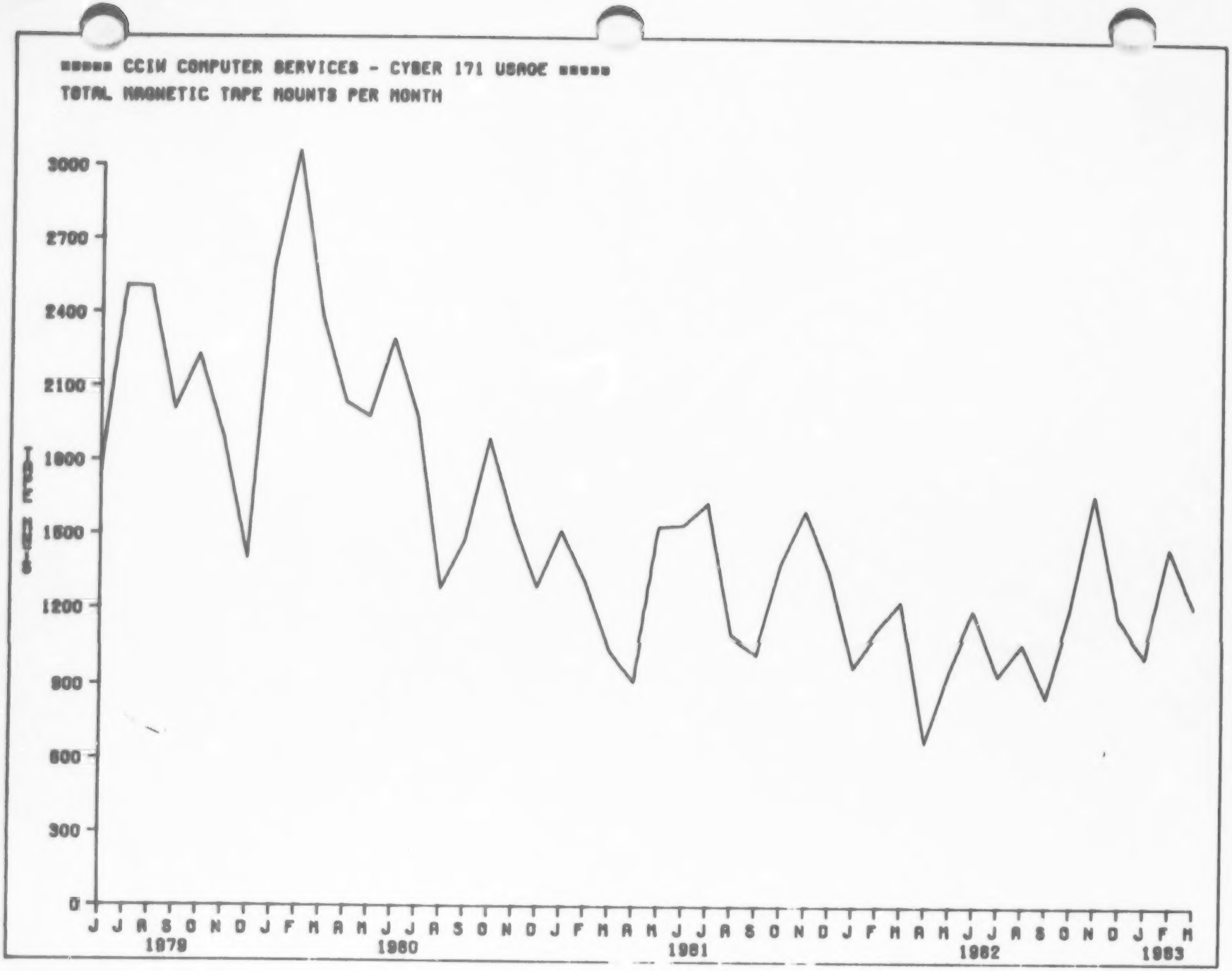
A set of graphs displaying many aspects of Cyber 171 utilization is attached.

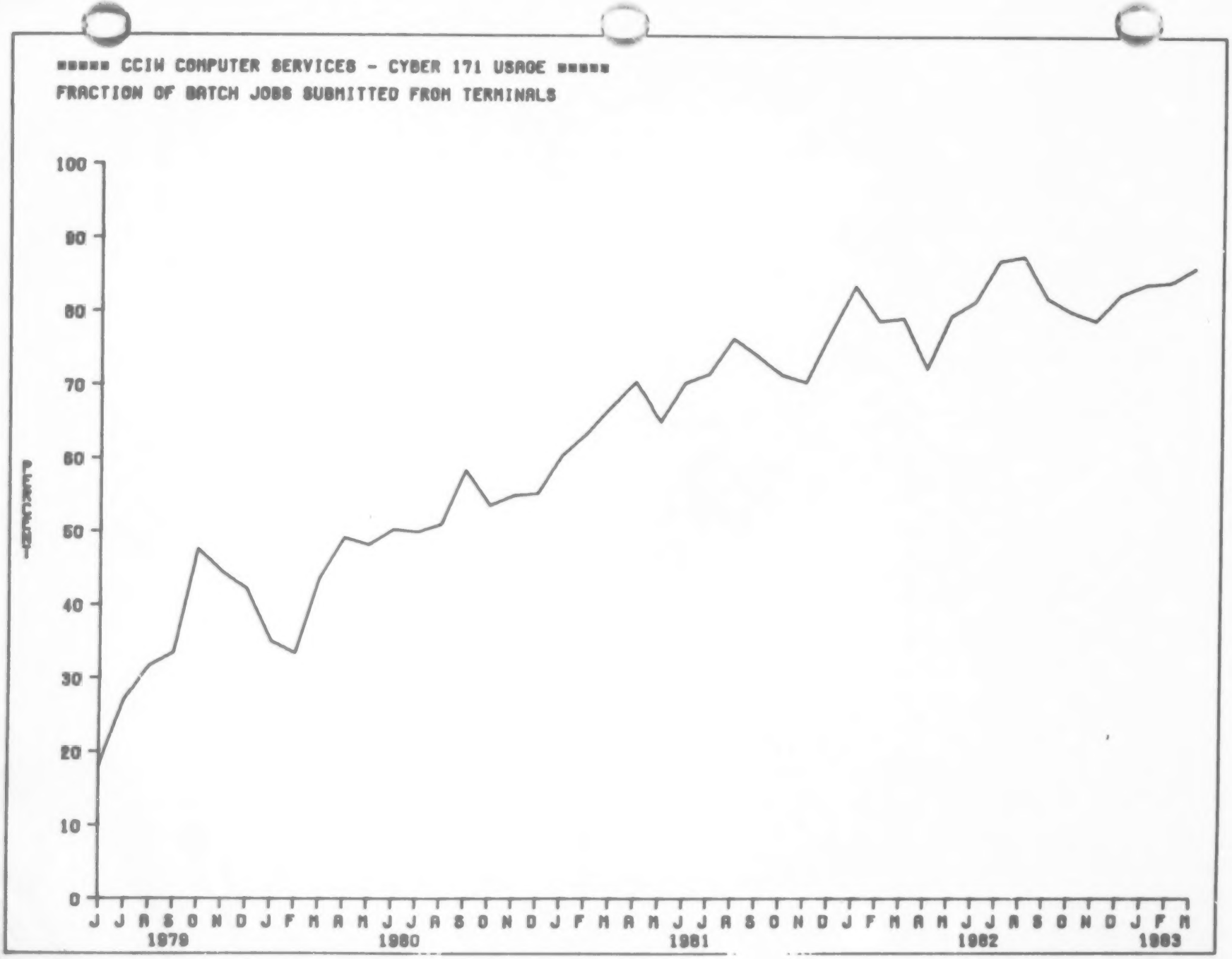

***** CCIW COMPUTER SERVICES - CYBER 171 USAGE *****
TOTAL JOBS/SESSIONS PER MONTH
BATCH
INTERACTIVE
COMBINED
JOBS-1000
10
9
8
7
6
5
4
3
2
1
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983

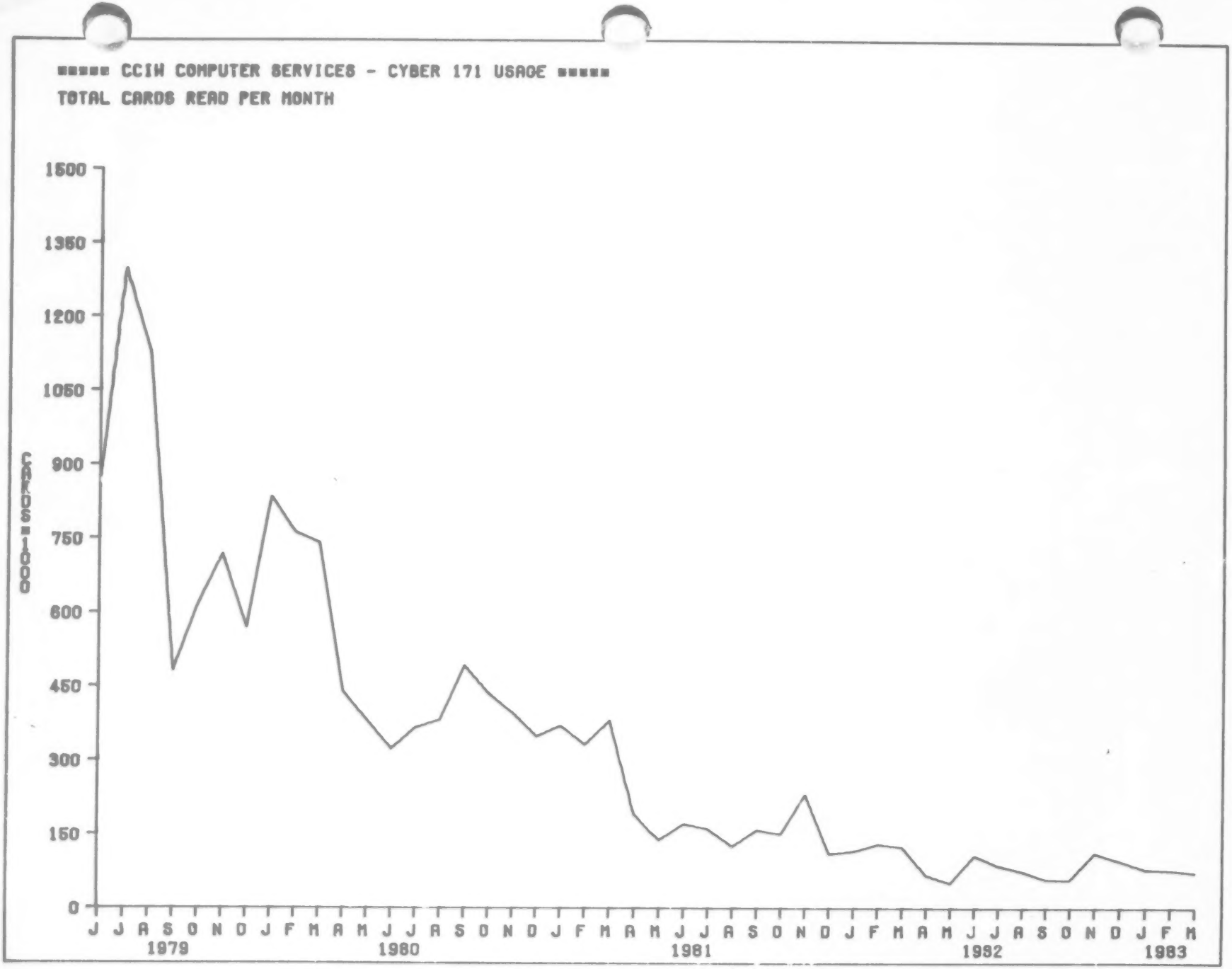

***** CCIM COMPUTER SERVICES - CYBER 171 USAGE *****
TOTAL CENTRAL PROCESSOR USAGE PER MONTH
BATCH
INTERACTIVE
COMBINED
CPU SECS
500
450
400
350
300
250
200
150
100
50
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A
1979
1980
1981
1982
1983

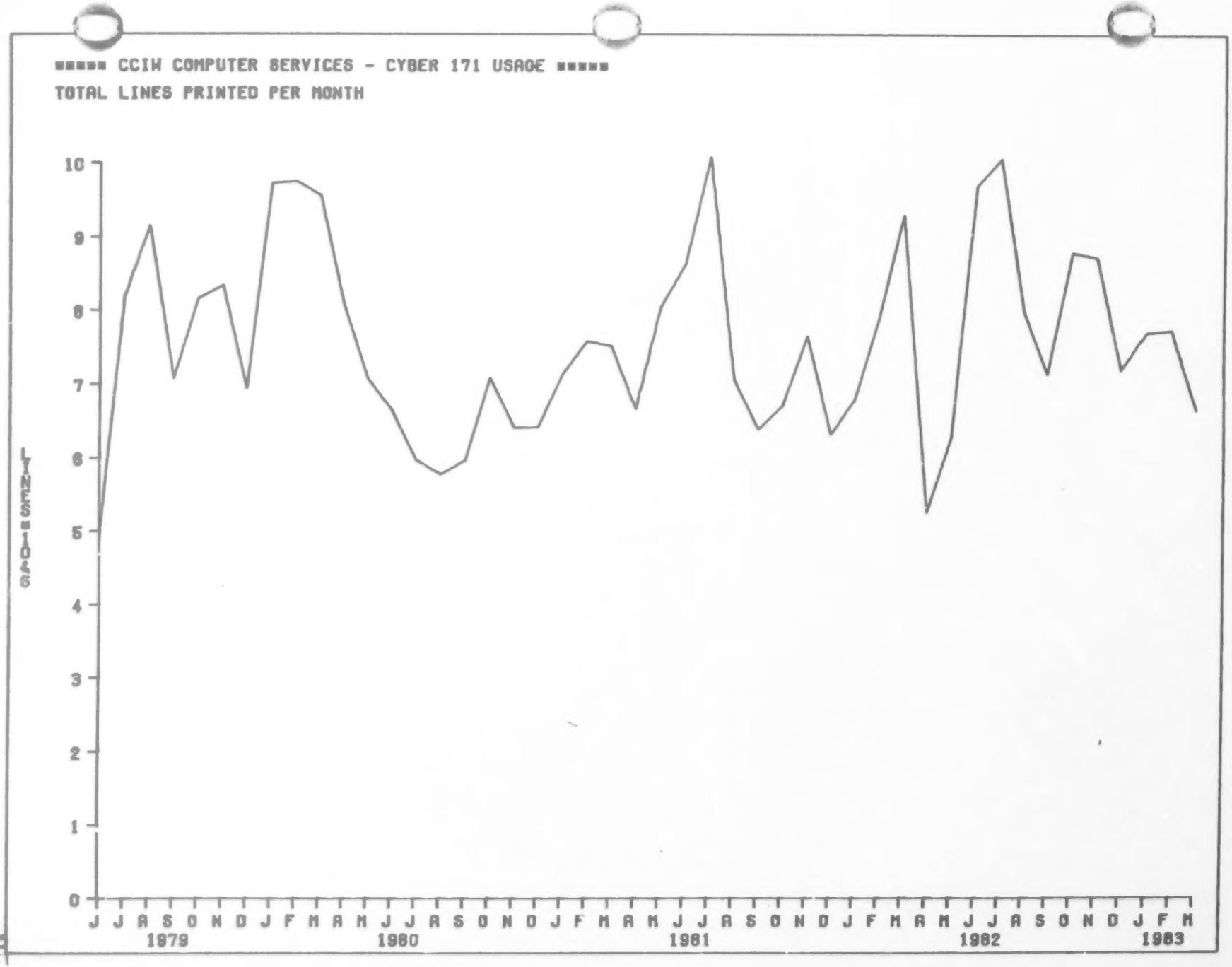

CCIN COMPUTER SERVICES - CYBER 171 USAGE
TOTAL CENTRAL MEMORY USAGE PER MONTH
BATCH
INTERACTIVE
COMBINED
30
27
24
21
18
15
12
9
6
3
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983

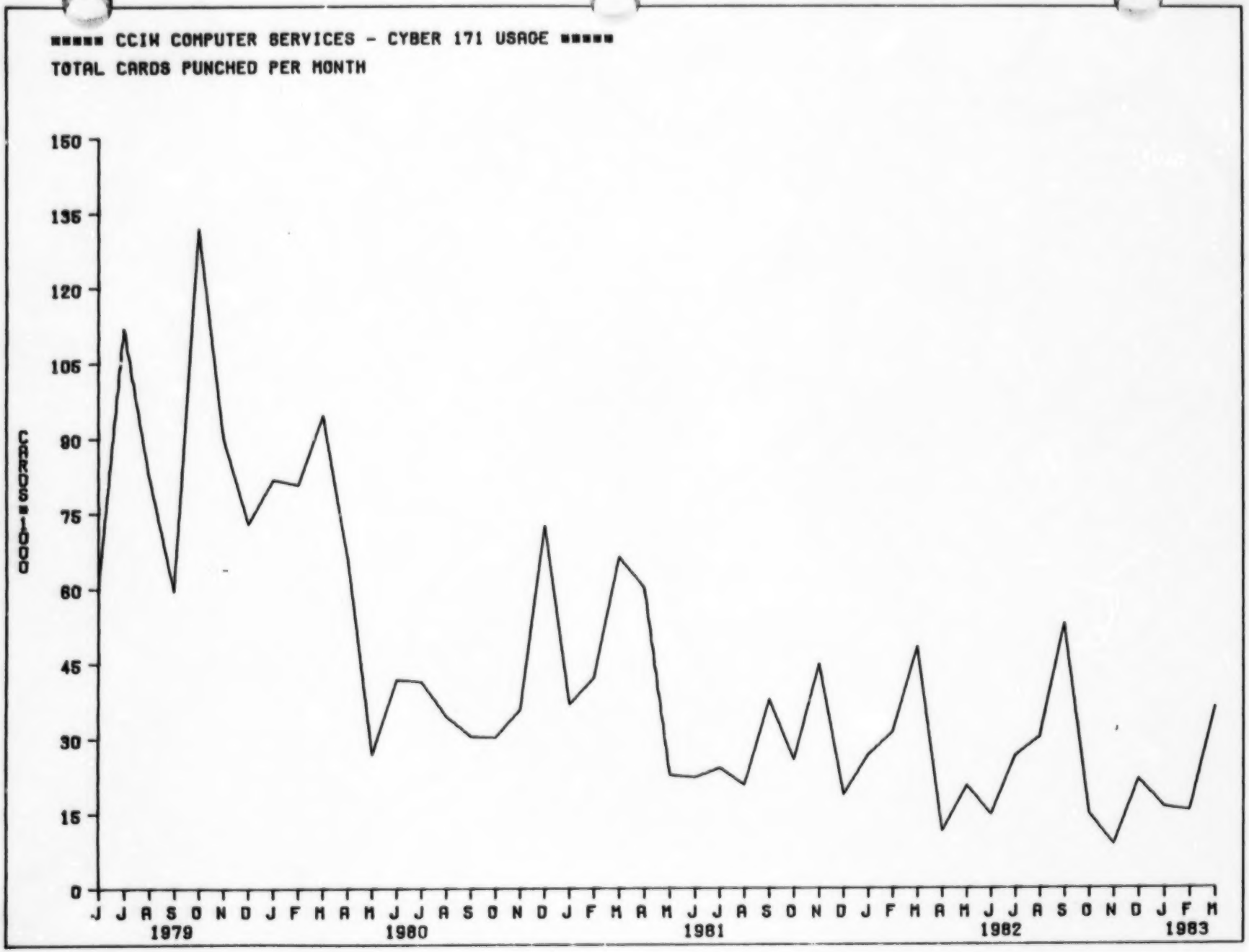

***** CCIW COMPUTER SERVICES - CYBER 171 USAGE *****
TOTAL INTERACTIVE CONNECT TIME PER MONTH
2000
1800
1600
1400
1200
1000
800
600
400
200
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983

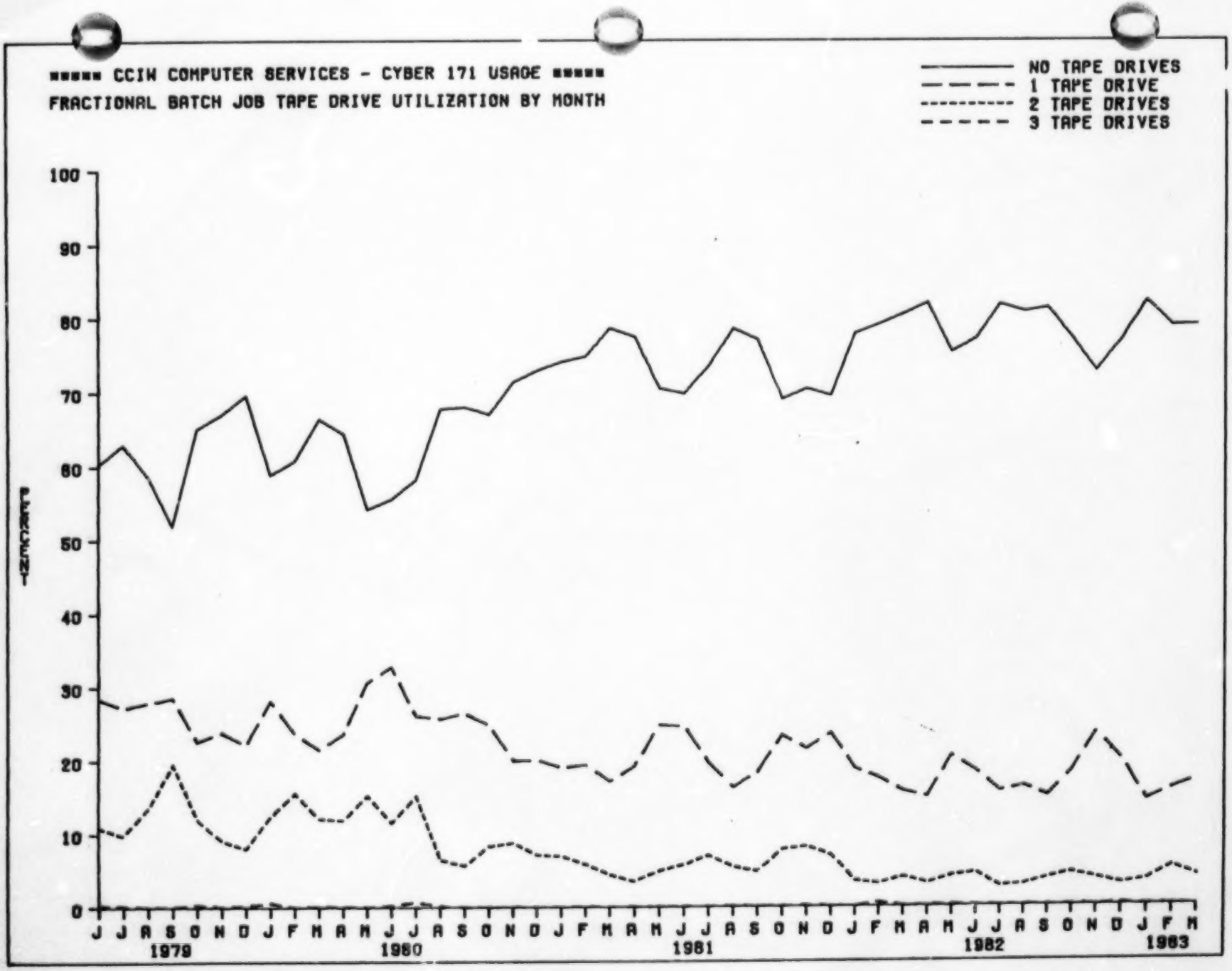

***** CCIW COMPUTER SERVICES - CYBER 171 USAOE *****
TOTAL MAGNETIC TAPE MOUNTS PER MONTH
TOTAL MTS
3000
2700
2400
2100
1800
1500
1200
900
600
300
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983

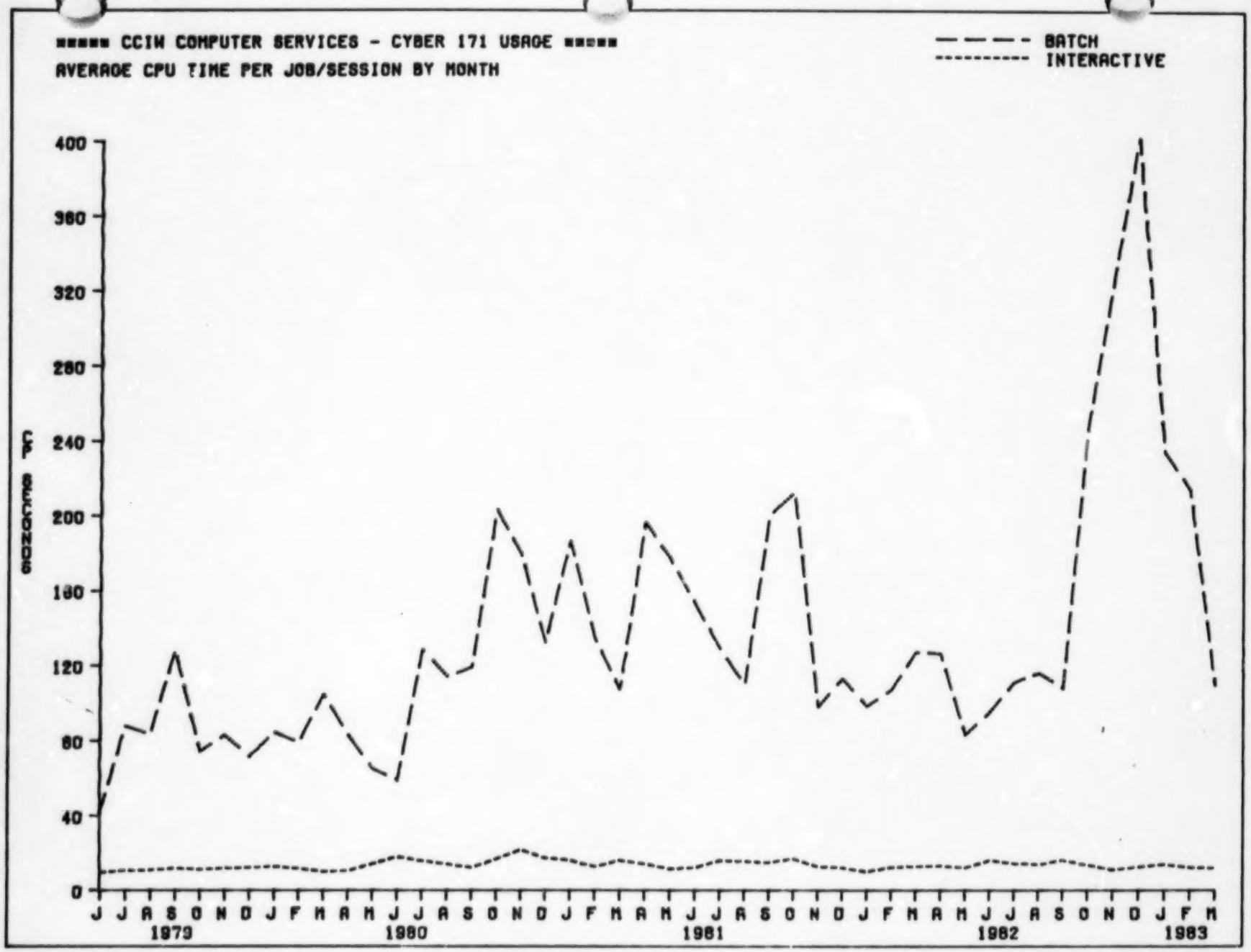

CCIW COMPUTER SERVICES - CYBER 171 USAGE
FRACTION OF BATCH JOBS SUBMITTED FROM TERMINALS
100
90
80
70
60
50
40
30
20
10
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983

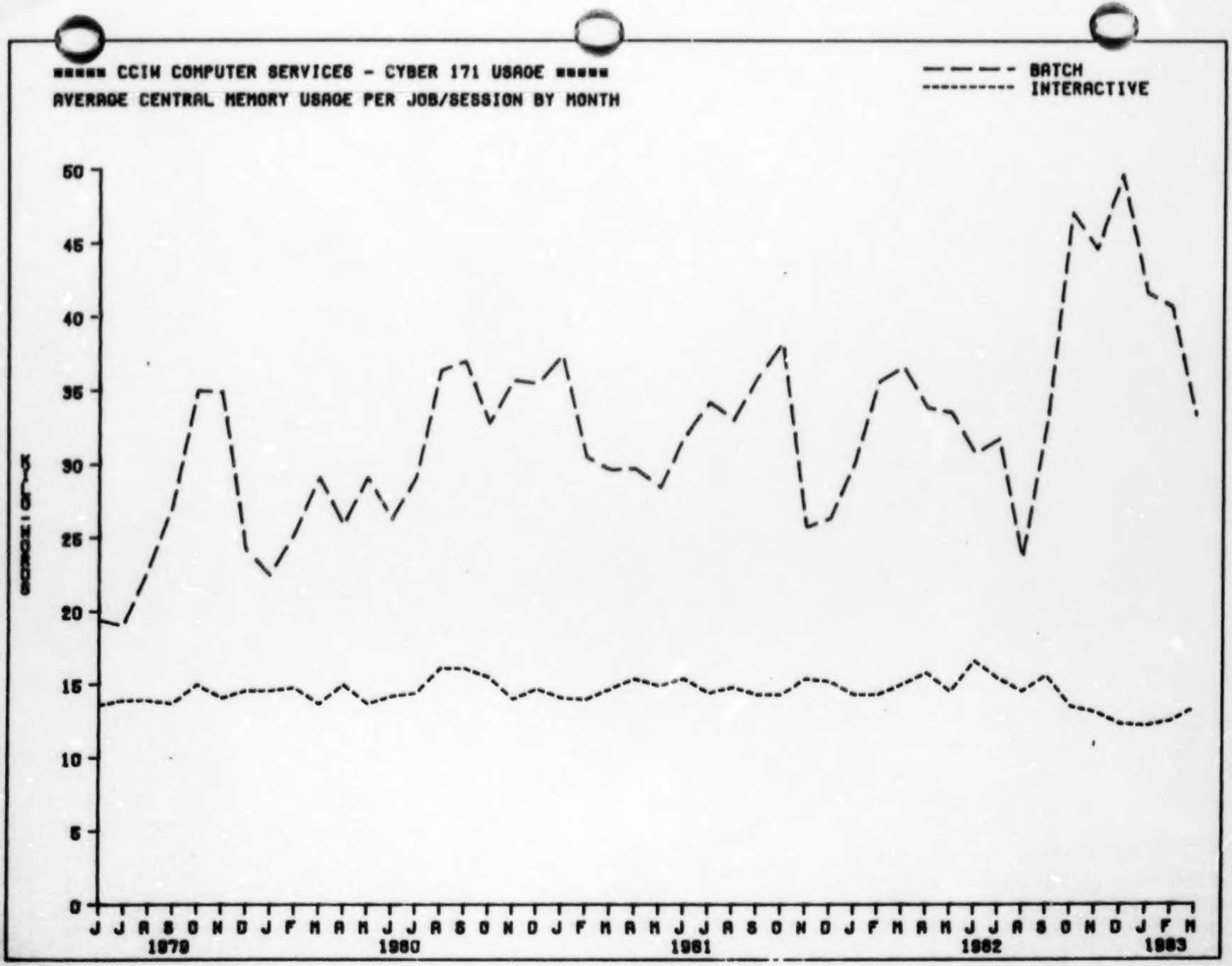

■■■■■ CCIW COMPUTER SERVICES - CYBER 171 USAGE ■■■■■
TOTAL CARDS READ PER MONTH
1500
1350
1200
1050
900
750
600
450
300
150
0
CARDS=1000
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983

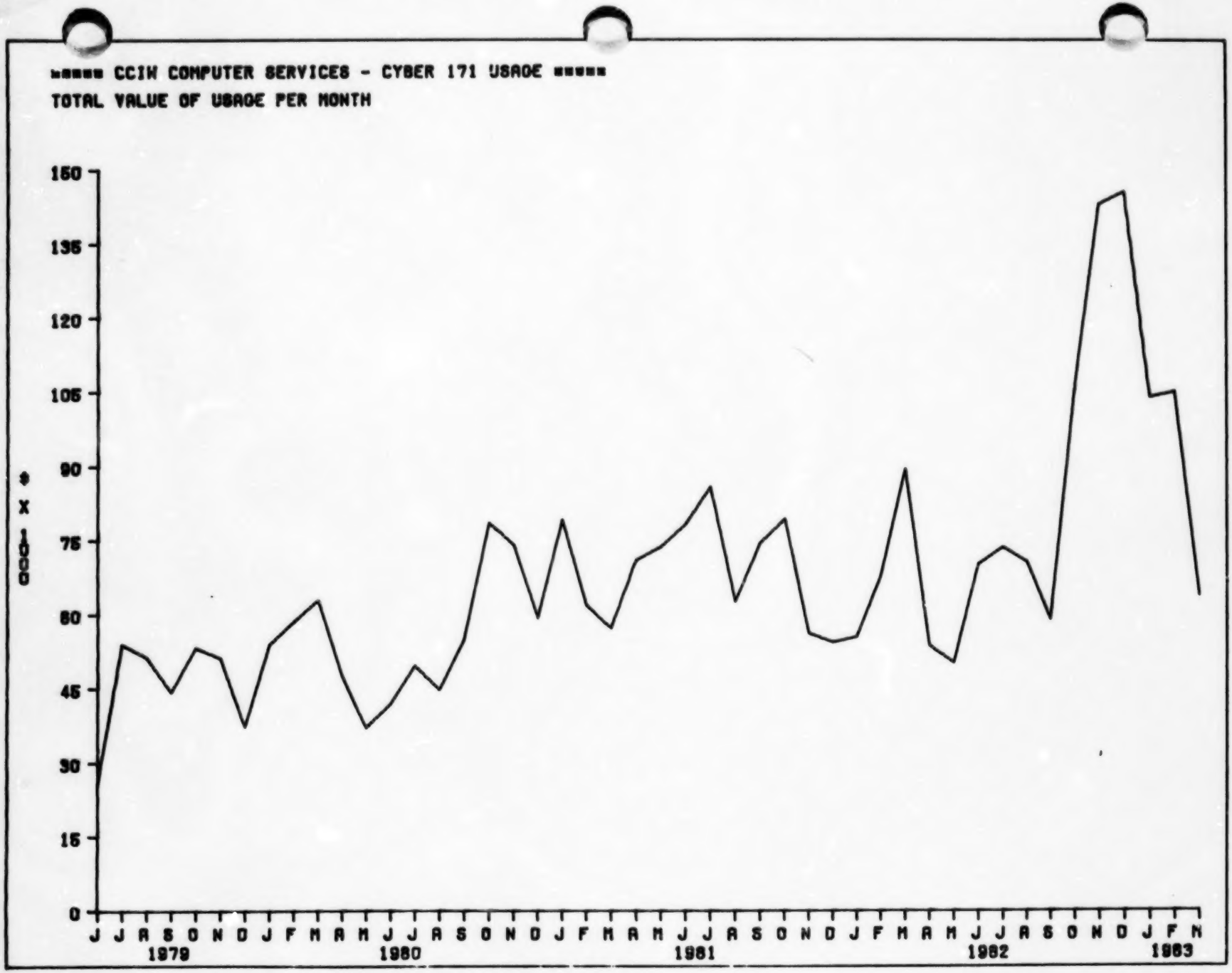

■■■■■ CCIW COMPUTER SERVICES - CYBER 171 USAGE ■■■■■
TOTAL LINES PRINTED PER MONTH
LINES*10^6
10
9
8
7
6
5
4
3
2
1
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983

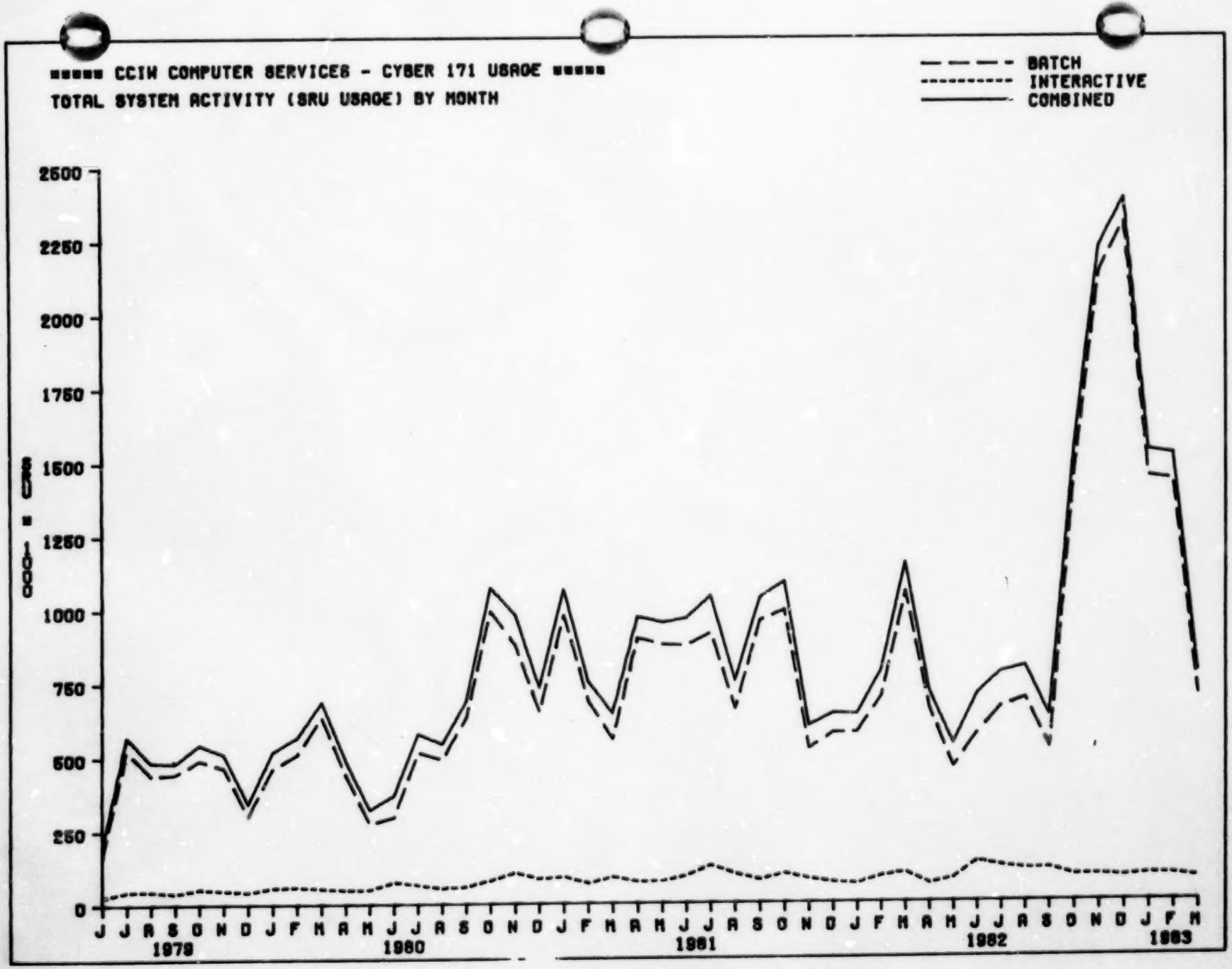

***** CCIW COMPUTER SERVICES - CYBER 171 USAGE *****
TOTAL CARDS PUNCHED PER MONTH
CARDS PUNCHED
000-0000
150
135
120
105
90
75
60
45
30
15
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983


***** CCIW COMPUTER SERVICES - CYBER 171 USAGE *****
FRACTIONAL BATCH JOB TAPE DRIVE UTILIZATION BY MONTH
NO TAPE DRIVES
1 TAPE DRIVE
2 TAPE DRIVES
3 TAPE DRIVES
100
90
80
70
60
50
40
30
20
10
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983


CCIW COMPUTER SERVICES - CYBER 171 USAGE
AVERAGE CPU TIME PER JOB/SESSION BY MONTH
BATCH
INTERACTIVE
CPU SECONDS
400
360
320
280
240
200
160
120
80
40
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983


***** CCIM COMPUTER SERVICES - CYBER 171 USAGE *****
AVERAGE CENTRAL MEMORY USAGE PER JOB/SESSION BY MONTH
BATCH
INTERACTIVE
KILOWORDS
50
45
40
35
30
25
20
15
10
5
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983


***** CCIW COMPUTER SERVICES - CYBER 171 USAGE *****
TOTAL VALUE OF USAGE PER MONTH
$ X 1000
150
135
120
105
90
75
60
45
30
15
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983


CCIW COMPUTER SERVICES - CYBER 171 USAGE
TOTAL SYSTEM ACTIVITY (SRU USAGE) BY MONTH
BATCH
INTERACTIVE
COMBINED
2500
2250
2000
1750
1500
1250
1000
750
500
250
0
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
1979
1980
1981
1982
1983

CANADA CENTRE FOR INLAND WATE[illegible] CYBER 171 COMPUTER SYSTE[illegible]

UTILIZATION STATISTIC[illegible] FISCAL 1982/83

YEAR	MONTH	OPN HRS	BATCH JOBS	BATCH CPU HR	BATCH JOB TM	BATCH S P U	INTERACTIVE SESS	INTERACTIVE CPU HR	INTERACTIVE CON HR	INTERACTIVE S P U	CARDS READ	LINES PRINTED	CARDS PNCHD	TAPE MNTS
82	04	350.9	3047	187.113	1304.22	657042.6	3349	12.055	1007.55	58807.1	66652	5256557	11325	672
82	05	348.2	3256	74.762	479.71	456166.3	4934	10.411	1426.86	78615.2	51279	6201471	24351	965
82	06	470.7	4159	181.629	1391.42	577077.2	6366	29.603	2023.46	134776.6	107119	8743280	34963	1198
82	07	390.9	4473	134.177	2774.45	662356.0	6232	25.104	2023.33	113916.4	86080	10065550	26390	944
82	08	376.6	4760	155.976	1015.36	691171.5	6038	23.075	1917.55	108952.6	74551	7985672	30244	1073
82	09	421.6	3584	109.728	873.94	520025.5	5060	22.414	1605.79	110315.6	58815	7136318	52703	857
82	10	501.7	4260	232.121	2204.79	1451774.1	4844	14.139	1565.35	86468.1	58269	6793949	14712	1280
82	11	449.9	4314	476.852	2157.38	2139741.1	5977	15.035	1867.74	87296.9	112485	8724243	8795	1557
82	12	442.6	4125	467.468	1515.19	2307222.4	4926	16.872	1541.34	81770.9	96571	7204879	21865	1171
83	01	481.7	4491	441.746	1064.48	1443334.7	4937	13.747	1624.32	88816.6	78973	7713229	16198	1026
83	02	350.8	4924	292.420	3816.31	1431078.7	5540	10.580	1769.11	89264.1	77463	7732285	15405	1456
83	03	358.6	4467	136.260	1051.00	701100.2	4891	16.051	1489.96	76912.5	72876	6650608	35978	1215
* TOTALS *		5803.1	50328	2596.020	19857.42	13032880.3	63246	234.083	19964.36	1119913.6	941093	93263721	268669	13448

OVERALL UTILIZATION - CPU 2830.10 HOURS. ELAPSED TIME 39021.79 HOURS. SRU COUNT 14151913.9 SRU. TOTAL JOBS/SESSIONS 113566.

VALUE OF CYBER 171 USAGE - BATCH $ 651600.81 INTERACTIVE $ 229343.64 PERIPHERAL $ 162250.02 OVERALL $1043193.67

AVERAGE CPU TIME - PER BATCH JOB 185.72 SECONDS. PER INTERACTIVE SESSION 13.32 SECONDS.

AVERAGE ELAPSED TIME PER BATCH JOB 22.72 MINUTES. AVERAGE CONNECT TIME PER INTERACTIVE SESSION 18.94 MINUTES.

AVERAGE SRU COUNT - PER BATCH JOB 259.0 SRU. PER INTERACTIVE SESSION 17.7 SRU.

CENTRAL MEMORY USAGE - BATCH, 146784. KWORD-HOURS, AVG CM/JOB 39.7 KWORDS. INTERACTIVE, 6265. KWORD-HOURS, AVG CM/SESS 14.[illegible] KWORDS.

CARD READER USAGE - BATCH, 8817 JOBS (17.5%) USED CR. AVG CARDS 106.
LINE PRINTER USAGE - BATCH, 41[illegible] JOBS (82.[illegible]%) USED LP. AVG LINES 1733. INTERACTIVE, 12084 SESS (19.1%) USED LP. AVG LINES 1742.
CARD PUNCH USAGE - BATCH, 175 JOBS (.3%) USED PC. AVG CARDS 203. INTERACTIVE, 413 SESS (.7%) USED PC. AVG CARDS 524.

MAGNETIC TAPE DRIVE USAGE - BATCH, [illegible]1 JOBS (78.7%) USED 0 DRIVE(S) CPU USAGE = 2369.2 HRS, 91.3% OF BATCH.
MAGNETIC TAPE DRIVE USAGE - BATCH, 4829 JOBS (17.[illegible]%) USED 1 DRIVE(S) CPU USAGE = 227.2 HRS, 8.[illegible]% OF BATCH.
MAGNETIC TAPE DRIVE USAGE - BATCH, 1[illegible] JOBS (3.[illegible]%) USED 2 DRIVE(S) CPU USAGE = 60.6 HRS, 2.[illegible]% OF BATCH.
MAGNETIC TAPE DRIVE USAGE - BATCH, 22 JOBS (.0%) USED 3 DRIVE(S) CPU USAGE = 1.0 HRS, .0% OF BATCH.
MAGNETIC TAPE DRIVE USAGE - BATCH, 0 JOBS (0.0%) USED 4 DRIVE(S) CPU USAGE = 0.0 HRS, 0.0% OF BATCH.